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Hazardous Waste Disposal Program Seventh Monthly Report

TRW Systems Group

Prepared For
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ONE SPACE PARK • REDONDO BEACH, CALIFORNIA

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HAZARDOUS WASTE DISPOSAL PROGRAM
SEVENTH MONTHLY REPORT

CONTRACT 68-03-0089

Prepared for
the
Environmental Protection Agency

10 August 1972

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The principle objective of the current program is to define and evaluate the waste management techniques and policies currently used for a specified set of hazardous wastes. Waste management techniques which will be evaluated include those for storage, handling, transport, neutralization, detoxification, reuse, and disposal. Other aspects of the program include description of possible new techniques for management of hazardous wastes, proof-of-principal experimentation to determine the effectiveness of techniques for which insufficient data is available for adequate evaluation, and planning of research programs necessary for developing new procedures and processes for treating hazardous wastes for which adequate techniques do not currently exist. The specific areas addressed were: 1) treatment process reports; 2) profile reports; and 3) determination of the forms and quantities of hazardous wastes.

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HAZARDOUS WASTE DISPOSAL PROGRAM

SEVENTH MONTHLY REPORT

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1. INTRODUCTION

Under the requirements of Section 212 of Public Law 91-512, The Office of Solid Waste Programs of the Environmental Protection Agency is in part required to prepare "a comprehensive report and plan for the creation of a system of national disposal sites for the storage and disposal of hazardous wastes, including radioactive, toxic chemical, biological, and other wastes which may endanger public health or welfare. Such a report shall include: 1) a list of materials which should be subject to disposal in any such site; 2) current methods of disposal of such materials; 3) recommended methods of reduction, neutralization, recovery, or disposal of such materials.

Contract 68-03-0089 is the second in a series of EPA projects which are designed to provide the information required in the report to Congress. The principle objective of the current program is to define and evaluate the waste management techniques and policies currently utilized for a specified set of hazardous wastes. Waste management techniques which will be evaluated include those for storage, handling, transport, neutralization, detoxification, reuse, and disposal. Other aspects of the program include description of possible new techniques for management of hazardous wastes, proof-of-principal experimentation to determine the effectiveness of techniques for which insufficient data is available for adequate evaluation, and planning of research programs necessary for developing new procedures and processes for treating hazardous wastes for which adequate techniques do not currently exist.

The seventh montnly technical report summarizes the work performed by TRW for EPA from July 1, 1972 to July 31, 1972 under Contract 68-03-0089.

2. PROGRAM ACCOMPLISHMENTS

The program is divided into seven major tasks consisting of:

- Defining Adequate Waste Management. Toxicity information and toxicological standards on each hazardous material contained in lists supplied by the Solid Waste Research Office will be reviewed. Other factors (such as flammability or explosive potential) which affect the waste management process will be investigated where applicable. Acceptable criteria in terms of impact on mankind and the environment for each of the waste management steps (handling, storage, transportation, disposal, etc.) shall be defined.
- Evaluating Presently Employed Waste Management Techniques or Policies and Making Recommendations as to Adequacy. The existing techniques for waste management of each hazardous material (supplied as in Task 1) will be assessed in relation to the criteria defined in the first task. Adequate techniques shall be recommended in order of preference and any required state-of-the-art modifications prescribed. Techniques which are applicable to national disposal sites will be specified.
- Performing Field Surveys and Verification Experiments on Existing Management Procedures. In cases where adequate information to determine the effectiveness of a particular waste management technique are not available, special field surveys or verification experiments will be performed. Results of those studies will be recycled to Task 2 to complete the evaluation of the particular hazardous waste material.
- Defining, Planning and Outlining Research Programs Where Necessary for Elimination of Hazards. Where no acceptable waste management techniques currently exist for a particular hazardous waste material, efforts will be made to innovate new approaches and the necessary research and/or demonstration programs will be planned and outlined. Prioritization of the programs in terms of importance of the problem and probability of success will be accomplished.
- Conducting Proof-of-Principle Experimentation on the Most Promising Concepts. Within the constraints of schedule and budget, proof-of-principle type experimentation will be conducted on the most promising but unproven concepts.

- Determining Waste Forms. Additional information on the hazardous waste materials designated under the earlier tasks as candidates for National Disposal Sites will be collected, analyzed and presented as an integral part of this program. This information will include the forms in which the wastes are found, their location, and the quantities of waste material generated.
- Correlating Total Program Effort. The program is directed to provide inputs to a final report which will: 1) summarize the best available waste management techniques for each material; 2) list on a prioritized basis those techniques to be included at possible National Disposal Sites; and 3) indicate major gaps in current hazardous waste management technology and provide a comprehensive, prioritized research and development plan for obtaining the required technology.

During July effort was concentrated primarily on Tasks 1, 2, and 6 of the program. The specific areas addressed were: 1) treatment process reports; 2) profile reports; and 3) determination of the forms and quantities of hazardous wastes. These efforts are discussed in the following sections.

2.1 TREATMENT PROCESS REPORTS

As was anticipated last month brief Treatment Reports for the various exhaust gas cleaning devices were prepared during July to provide more complete background for the incineration processes and other processes with which they are normally utilized. Air correction equipment described includes wet collection equipment such as: spray towers/chambers, packed bed scrubbers, wet cyclone scrubbers, self-induced spray scrubbers, orifice plate bubblers, venturi scrubbers, jet scrubber, and dynamic wet scrubbers and dry removal systems such as: mechanical collectors; electrostatic precipitators, and fabric filters. A treatment process report was prepared for radioactive waste solidification processes. These processes are intended to replace the currently utilized storage of liquid and loose solid radioactive waste materials. The above described reports are presented in Appendix A.

2.2 PROFILE REPORTS

During the last month, profile reports for 32 chemical compounds were completed. The reports on the chemical hazardous wastes completed during July are listed below and presented in Appendix B.

Hazardous Material Number	Hazardous Material Name
81,82,83,85,86,479,480,481	Cadmium, Cadmium Powdered, Cadmium Chloride, Cadmium Oxide, Cadmium Phosphate, Cadmium Nitrate, Cadmium Potassium Cyanide, Cadmium Sulfate.
107,422	Chloroacetophenone, Tear Gas
112	Chlorosulfonic Acid
233	Lead
253,255,256,257,503	Mercuric Chloride, Mercuric Nitrate, Mercuric Sulfate, Mercury, Mercuric Diammonium Chloride.
290,296,298,347	Nickel Amonium Sulfate, Nickel Nitrate, Nickel Sulfate, Potassium Permanganate
291,292,297	Nickel Antimonide, Nickel Arsenide, Nickel Selenide.
326	Perchloryl Fluoride.
385	Sodium Chlorate.
485,486,487	Chromic Fluoride, Chromic Sulfate, Chromium Cyanide.
499	Manganese.
502	Manganese Methylcyclopentadienyltricarbonyl.
528	Hydrazaic Acid.

Also completed during July were Profile Reports on 19 radioactive waste compounds. The remaining reports in this category will be completed during August. Those completed during July are listed below and the first draft reports are presented in Appendix C.

Hazardous Material

1. Cesium-134, Cesium-137, (Barium-137m)
2. Plutonium-238, Plutonium-239, Plutonium-240, Plutonium-241, Americium-241, Americium-243, Curium-242, Curium-244
3. Ruthenium-106 (Rhodium-106), Cerium-144 (Praseodymium-144), Promethium-147
4. Strontium-90
5. Zirconium-95, Niobium-95

2.3 IDENTIFICATION OF WASTE FORMS

The effort to identify the waste forms, locations and quantities for those hazardous wastes designated as candidates for the National Disposal Sites was begun during July. In recognition of the needs of the Feasibility Study a preliminary report summarizing the results of the first contract study and TRW's first estimates is planned. The required information will be prepared for inclusion in the 8th Monthly Report. During July contacts were made with major industry waste management organizations to provide data for input to this preliminary report.

3. WORK PLANNED FOR AUGUST

The Profile Report preparation for the Category 1 materials will continue into August. Sixty-seven chemical compounds remain to have Profile Reports prepared. As was mentioned earlier effort on the Profile Reports for the nuclear waste materials is also scheduled for completion during August as is a preliminary report summarizing waste quantities and locations. Effort is also expected to get under way on the proof-of-principal testing (Task 5) portion of the study. Under Task 5 two areas have been discussed with and approved by the project monitor: 1) removal of arsenic/mercury from contaminated solids; and 2) recovery of mercury from brine sludges.

APPENDIX A - PROCESS EVALUATION REPORTS

AIR CORRECTION EQUIPMENT

1. INTRODUCTION

The following is a discussion of the general types of air correction equipment currently employed for the control of gaseous and/or particulate pollutants in process effluent streams. There are currently two general categories of abatement equipment in use--wet collection equipment and dry collection equipment. This report will summarize the general operating principles, operational characteristics, and applications of the common types of pollution control equipment.

2. WET COLLECTION EQUIPMENT[2188,1673,2189]

In the collection of gaseous pollutants, the primary removal mechanism in wet collection systems is the absorption of the gaseous pollutant into water or other suitable solvents. The basic operation consists of the diffusion of the gas molecules to the water surface. Concentration differentials near the liquid/gas interface serve as the driving force. Control equipment which applies this principle is characterized by high interfacial surface areas, turbulence in the gas phase, and high diffusion coefficients. Fortunately, in the area of gaseous emission control, a great number of the most common gaseous chemical species have high solubility in water.

Particulate collection liquid scrubbers depend upon a somewhat different set of physical processes. The primary collection mechanism is the impaction of solid particulate material on liquid droplets generated in the scrubber. The function of the liquid scrubber is to generate and place in contact with the exhaust gas stream a sufficient number of liquid droplets in the appropriate droplet size range. Additional physical mechanisms by which particulate dispersoids are collected in wet scrubbers are Brownian diffusion, condensation of liquid on the particulate material, and agglomeration. In each case, the relative

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effective size of the particulate material is increased in the scrubber, thus facilitating its ultimate collection and disposal.

It should be noted that the mechanisms of gaseous and particulate collection in liquid collectors are somewhat different and that a liquid scrubber designed to maximize gaseous pollutant removal may be significantly less effective in the collection of particulate material. Application of scrubbers to specific industrial effluent cleaning tasks should be made only on the basis of careful consideration of the relative importance of the gaseous and particulate emissions and analysis of the particle size distribution in the effluent gas stream to be cleaned.

Spray Towers/Chambers

A chamber scrubber consists of a chamber into which the water or an aqueous solution is introduced through spray nozzles. The gas stream may make a single direct pass through the chamber, or the path may be controlled by a series of baffles. Several such chambers or scrubbers are often used sequentially to produce the desired degree of pollutant removal. These devices are characterized by a very low pressure drop for the gas phase (0.1 to 0.5 in. of water). Water pressure required for spray operation ranges from 20 to 100 lb per square in. Water consumption is usually in the range of 1/2 to 2 gal per 1,000 cubic feet of gas treated.[2188]

Spray chambers are used for the removal of both particulate and gaseous pollutants. The efficiencies of these devices are generally rather low for particulate materials and are suitable only for the removal of particulate materials 10 microns in size or larger. For the collection of smaller particulate material, very high water pressures have been successfully used. Water pressures on the order of 300 to 450 lb per square in. (psi) produce a fog spray which will achieve collection efficiencies of the order of 90 percent for particles in the 1 to 2 micron size range. The larger water pressure drops required to acheive high efficiency fog spray result in a proportionally higher pump horsepower and operating cost. Baffled spray chambers require higher gas velocities and result in greater gas pressure drops which, in turn, require greater fan horsepower to recover the lost pressure head and more expensive ductwork.

The simple spray chamber is often used effectively for gaseous pollution control, especially when treating some of the relatively more soluble pollutants. Surface contact area, an important consideration in gaseous absorption, is relatively low in spray chambers compared with other types of liquid scrubbers. For this reason, simple spray chambers must be very large to produce efficiencies equivalent to more sophisticated liquid collection systems. The overall efficiencies reported for multiple spray chamber installations are greater than 90 percent. There are no limitations on gas throughput volume other than those imposed by equipment size limits. However, gas flow rates of approximately 800 lb/hr-ft^2 have been demonstrated as the upper limit, to prevent excessive liquid entrainment.[1673]

Spray chambers or towers, because of their simple design, represent one of the most economical control devices to purchase and install. The operating and maintenance expenses associated with this type of device are also low because of the mechanical simplicity. Primary maintenance problems are caused by the use of small, high-pressure nozzles which may tend to clog under prolonged usage. The low pressure drops (generally less than 1 in. of water) allow the use of inexpensive ductwork and fans to convey the effluent gas stream to the collector.

Packed Bed Scrubbers

The packed bed scrubber is similar to the spray chamber described above in that the effluent gas stream to be cleaned is directed through a chamber or tower in which it makes contact with the scrubbing liquid. The high liquid surface area exposed to the gas stream is produced by interaction with the packed bed. The packed bed may be in the form of a fixed packing or loose material which is supported by the action of the gas stream passing through it. This latter type is called a floating bed scrubber. Scrubbing liquid is generally passed through this type of scrubber in a direction crosscurrent or countercurrent to the gas flow.

The fixed bed scrubber is not often used strictly for particulate pollutant collection. Operating problems have been encountered when this type of collector is utilized to clean a gas stream containing an excessively high concentration of particulate material. Therefore, in conjunction with this type of equipment, some form of dry collection equipment is used that eliminates much of the particulate load on the wet scrubber and helps prevent clogging.

The floating bed units, in which the packing is supported by the upward motion of the exhaust gas stream, are reported to be more resistant to clogging caused by particulate collection than the fixed packed bed units.[2186,0304] This reported increased ability to handle particulate contaminant is attributed to the relative motion between the packing materials which produces a self-cleaning action and allows the collected particulate material to be removed by the liquid flow. High particulate removal efficiencies (95 to 98 percent) have been reported for floating bed scrubbing units.

A condition known as flooding occurs when the upward gas velocity in the packed tower reaches a point at which there is a hold-up of liquid phase on the packing. In this condition, the liquid held in the packing builds up and eventually increases the pressure drop across the packed tower unit to the point where liquid will be entrained and carried out with the exhaust stream. Care must be taken in the design and operation of tower equipment to ensure that this flooding condition is avoided and a reasonable pressure drop is maintained. Properly designed packing materials allow a high liquid surface area to be maintained within the scrubber. Operation at proper liquid-to-gas flow ratios can achieve high gaseous pollutant removal at relatively low gas flow resistances. Packing materials commonly used are plastic materials of various shapes, including rings, spiral rings, berl saddles, and other shapes which allow a high ratio of surface area to volume.

Utility consumption for the packed bed scrubber depends on the design of the bed, the packing material used and the collection efficiency desired. Typical water consumption for the packed bed scrubber ranges from

5 to 10 gpm per 1,000 CFM. Normal packed scrubber design dictates a pressure drop of from 1 to 10 in. of water with a total horsepower requirement of 0.3 to 2.8 for fan and pumping costs. Efficiencies of 95 to 98 percent have been realized for both particulate and gaseous control, although not necessarily concurrently.

The choice between crossflow and countercurrent scrubber design is dependent on the particular application. However, generally the crossflow scrubber is applied to situations where the bed depth is less than 6 ft and countercurrent design is applied at bed depths of 6 ft or more. These applications are based on the lowest combination of installed capital cost and operating cost.

Wet Cyclone Scrubbers

Wet cyclones are characterized by tangential entry of the air stream to be cleaned. The air stream passes through the collector in a spiral path. The liquid stream is directed outward from the center of the circular collection chamber. The cyclonic scrubber thus possesses some of the characteristics of both the simple dry cyclone collector and the spray chamber.

Particulate collection is accomplished by combining centrifugal acceleration of the particles toward the chamber wall with the action of the spray droplets in contacting and removing the particle. Particulate collection efficiences are generally in excess of 90 percent for particles 5 microns or larger. Gaseous pollutant capture is produced by the intimate turbulent contact between the exhaust gas stream and the liquid particles generated by spray nozzles and air stream shear forces within the scrubbing unit. Liquid requirements are generally on the order of 2 to 10 gal of water per 1,000 cubic feet of gas treated. Gaseous collection efficiencies range up to 99 percent with pressure drops of 1 to 8 in. of water. Total fan and pump horsepower vary from 1 to 2 per 1,000 CFM. Wet cyclones have been designed to treat up to 100,000 CFM.

In summary, the wet cyclone has desirable characteristics when the gas stream to be cleaned contains both particulate and gaseous materials. The wet cyclone has an adequate capacity for handling high input dust loadings and produces acceptable collection efficiencies for both medium sized (>5 microns) particulate and gaseous pollutants. Where extremely high particulate collection efficiencies are required, however, the wet cyclone is used in conjunction with higher efficiency collection units. The purcahse, installation and operating costs associated with cyclonic scrubbers are comparable with those of packed bed units for situations where the exhaust gas stream to be cleaned represents a high gas flow rate; however, the cyclonic scrubber requires less maintenance.

Self-Induced Spray Scrubbers

In this type of scrubber, the gas liquid contact is created as a result of impingement of the carrier gas upon a liquid. The performance characterisitics are thus dependent upon the gas flow rate through the collector. The effluent gas stream to be cleaned is impinged upon the surface of the scrubbing liquid; the scrubbing liquid is fragmented and broken into droplet-sized particles by the kinetic energy in the gas stream. The liquid droplets formed are entrained, and the effluent gas stream is passed through further sections in which turbulent contact between the liquid and gas phases occur.

Particulate collection efficiency approaches 90 percent for particles 2 microns and larger. For medium efficiency collection units of this type, pressure drops range between 3 and 6 in. of water. The entrained water droplets and the collected particulate material are removed in the final demisting stage of the induced spray scrubber.[2187] This type of equipment is particularly applicable to gas streams with high dust loadings since continuous removal of sludge can be accomplished with the installation of a screw convenyor. No pumping horsepower is required since the water remains at essentially atmospheric pressure and is atomized by the gas stream.

Another advantage of the induced spray collector lies in the fact that construction does not involve close clearances or small orifices. Clogging, which often represents the bulk of the maintenance problems in wet collectors, would not be expected under normal operating conditions.

Gaseous collection efficiency in the self-induced spray scrubber has been reported to be greater than 99 percent removal. The control system reported in these observations was a two-stage scrubbing operation with sequential induced spray collectors. Liquid-to-gas requirements are generally lower for this type unit than for most other wet collectors. Liquid requirements range between 1/4 to 3 gal of liquid per 1,000 cubic feet of gas. Fan horsepower for head recovery is from 0.7 to 1.4 per 1,000 CFM of treated gas.

Orifice Plate Bubblers

The orifice plate bubbler is a class of wet impingement scrubber. The gas stream to be cleaned is passed through a perforated plate and impinged on baffles where the gas jets attain maximum velocity. The impingement baffles are covered by a layer of scrubbing liquid during operation. The gas stream passing through the baffle plate prevents the flow of liquid through the perforated plate. Intimate mixing of the gas streams and the liquid occurs facilitating both gas transfer to the liquid phase and particulate collection by the scrubbing liquid.

Particulate collection efficiencies from 90 to 95 percent have been reported for 2-micron diameter dust particles. Several stages of perforated plate and impingement baffle may be assembled into a single collector unit. The particulate removal efficiency is directly related to the number of plates used in the scrubber. As is usual in the design of wet collectors, a mist eliminator is used following the last baffle plate section. Pressure drop through the impingement baffle system has been reported between 1 to 10 in. of water depending upon the size and number of perforations used, and the number of impingement plates in the collector.[2188]

Gaseous pollutant removal efficiencies between 99 and 99.5 percent have been reported for orifice plate bubblers. High collection efficiencies for both particulate and gaseous pollutants make this unit applicable in a wide range of control situations. Water usage runs from 1 to 5 gpm per 1,000 CFM and the total (fan and pump) horsepower requirements range from 0.5 to 3 per 1,000 CFM.

Clogging has not proved to be a problem in this equipment even though the perforations in the plate are typically only 1/4 in. or less in diameter. Clogging is prevented by high (75 ft/sec or more) gas velocities through these orifices which agitate the liquid on the surface of the plate and keep the dust particles in suspension.

Venturi Scrubbers

The basic distinguishing design feature of the venturi scrubber is the passage of the exhaust gas stream through a venturi-type constriction. In this constriction, high linear gas velocities on the order of 12,000 to 42,000 ft per minute are attained. The scrubbing liquid is usually introduced normal to the gas flow at or near the minimum flow area of the venturi. The high gas velocity at this point atomizes the scrubbing liquid into fine droplets that are maintained in turbulent contact with the gas stream.

Particulate collection efficiencies in the venturi scrubber are directly related to the gas phase energy input. Gas pressure drops of 10 to 100 in. of water are common in this type unit with particulate collection efficiency for submicron particles approaching 99 percent at the higher pressure drops. The freedom from clogging afforded by the relatively simple liquid distribution system of this type unit makes possible the treatment of exhaust streams containing high dust loads. The high particulate removal efficiency further makes the venturi scrubber most applicable when particulate removal is of primary importance.

The intimate gas-liquid contact obtained in this type unit allows the efficient removal of gaseous as well as particulate pollutants. Gaseous pollutant removal efficiencies from 80 to 99 percent have been reported. The venturi pressure drops associated with these reported efficiencies ranged from 15 to 50 in. of water.[2188] Scrubber liquid requirements for this type of control equipment range from 3 to over 8 gal per 1,000 cubic feet of gas.

Jet Scrubber

Another type of scrubber operated on the venturi principle is the jet scrubber or ejector venturi design. As in the case of the standard venturi scrubber, the basic operating principle consists of passage of the exhaust gas flow through a restrictive orifice. In the ejector venturi design, the energy impelling the gas stream through the orifice comes from a high pressure liquid spray rather than from the gas phase pressure drop across the collecting unit i.e., water is used to aspirate the dust-laden gas through the ejector. The ejector provides the head for the gas, although large induced drafts (above several inches of water) are usually avoided to maintain a high entrainment ratio since larger entrainment ratios require less water for a given gas flow rate. Typical water usage ranges from 50 to 100 gpm per 1,000 CFM with a pressure drop of 50 to 100 psi for the water across the ejector. This amounts to 1 to 5 pump hp per 1,000 CFM. Particulate and gaseous collection efficiencies experienced with the ejector venturi design are comparable with those attained in conventional venturi scrubbing. In both devices, the air stream is brought into intimate and turbulent contact with a fine droplet spray.

The jet scrubber is usually followed by a baffled or settling chamber to capture the water treated particulate matter and water droplets. The main use for this type of equipment is in situations where it is not economical to add a fan to the system. A wide range of sizes is available in this type of collection unit and multiple banks of ejector venturis have been used to control large process emission sources.

Dynamic Wet Scrubbers

In the dynamic wet scrubber, liquid is mechanically sheared into fine droplets and then contacted with the dust laden gas stream. The shearing usually is accomplished by injecting the water into fan blades which simultaneously mix the water and dust streams and recover the lost pressure head of the effluent stream. The wetted impeller and a housing hold the collected dust particles and prevent re-entrainment. The dust collection efficiency is approximately 95 percent for 1 micron particles. Although no pressure drop is incurred by the process stream, there is a 3 to 20 hp/1,000 CFM requirement for the fan to disperse the water and recover the head. Many of the higher horsepower dynamic units are being displaced with venturi scrubbers. Typical water consumption varies from 3 to 5 gpm per 1,000 CFM. Good gaseous collection efficiencies can be expected from the dynamic wet scrubber because of an intimate mixing of the water and the process stream.

3. DRY REMOVAL SYSTEMS[2188,1673,218]

Dry removal systems are generally used as primary treatment systems and have little effect on gaseous pollutants. Under certain conditions, dry collection systems have been applied to effluent streams either to decrease the particulate load on subsequent control equipment or to collect a solid adsorbant that has been used to reduce the stream's gaseous pollutant content. In either case, the dry collection equipment is usually followed by secondary or even tertiary treatment. Three main classes of dry collection equipment are available: mechanical collection equipment, electrostatic precipitation, and fabric filtration.

Mechanical Collectors

Mechanical collectors (inertial separators) have proven to be reliable collectors of dry particulate material in a number of air pollution control applications. These devices collect particulate material by the use of centrifugal force, gravitational force, or by rapid changes in the direction of the dust laden stream. Mechanical devices are simple to construct, relatively inexpensive, and operate at moderate pressure drops. Generally, the efficiency of the mechanical collector will increase markedly with increased dust loadings, thus, it is often used as a precollector for more efficient control equipment which is susceptible to overload. Common types of dry mechanical collectors employed in industry include the settling chamber, the louver type collector, the cyclone, the impingement collector, and the dynamic collector.

Settling Chamber. The settling chamber directs the dust laden gas into an oversized duct where the gas velocity drops to a point where the entrained particles drop out because of the force of gravity. This type of equipment is used in relatively high particulate concentrations (above 5 grains/ft^3) with particles sizes of 50 microns or larger. Dust collection efficiencies range from 50 to 90 percent depending on dust particle size distribution. The pressure drop through the settling chamber ranges from 0.2 to 0.5 in. water gage (wg) resulting in a low fan horsepower requirement of 0.04 to 0.12 per 1,000 CFM of treated gas. Since the efficiency of the settling chamber is relatively low for dispersoid particulates and has no effect on gaseous pollutants, this type of equipment is generally used for pretreatment of a gaseous stream that is to be fed to some more efficient type of collection device. The volume of gas that is treated by this type of equipment is limited only by the space available for the unit designed to treat that volume. The typical gas velocity through the chamber ranges from 5 to 10 ft per second.

Baffle Chamber.[2189] In the baffle chamber, settling is aided by using the momentum of the heavy particulate matter to separate it from the carrier gas. The dust laden gas enters the baffle chamber and is directed downward around a baffle and out the top of the chamber. The heavy dust particles tend to continue moving downward and are separated from the gas stream. They drop out a small opening in the bottom of the chamber and are collected. The baffle chamber is used for the same type of conditions as is the settling chamber with the advantage of a smaller space requirement. Gas velocities of 20 to 40 ft per second are typical in the baffle chamber with a pressure drop of 0.1 to 0.5 in. of water. The fan horsepower requirement needed to compensate for this pressure drop is 0.02 to 0.12 per 1,000 CFM of treated gas. The baffle chamber has a collection efficiency of from 50 to

90 percent depending on the dust particles to be removed (usually above 50-micron diameter).

Skimming Chamber.[2189] The skimming chamber is similar to the baffle chamber in that it uses the greater momentum of the dust particles to separate them from the gas stream. The dirty gas stream enters an enclosed metal scroll tangentially and the dust is carried to the edge by inertia. A concentrated dust stream is skimmed from the edge of the scroll and sent to a secondary chamber. Gas velocities of 35 to 70 ft per second are typical for this type of equipment. Efficiencies of 70 percent are obtainable with particles 20 microns in diameter. Pressure drops of up to 1 in. of water can be expected with a resulting horsepower requirement of from 0.02 to 0.24 per 1,000 CFM. The limiting size for this type of equipment is 50,000 CFM.

Louver Type Collectors[2189] This type of equipment also employs the difference in momentum between the dust particles and the carrier gas to separate out the dust. The incoming gas must make a sharp bend in order to escape through the louver (slots) in the wall. The heavier dust particles are carried to the end of the apparatus where they are carried out by a small portion of the original gas stream in a concentrated stream. Efficiency of 80 percent can be obtained on 20-micron particles at gas velocities of 35 to 70 ft per second. Flow rates are limited to 30,000 CFM for this type of equipment. A pressure drop of 0.5 to 2 in. of water can be expected through this type of equipment requiring from 0.12 to 0.48 fan hp per 1,000 CFM to return the gas stream to pretreatment pressure conditions.

Dry Cyclones.[2189] In a cyclone, the dust laden gas enters the top of the apparatus tangentially, forming a vortex that extends downward toward the bottom of the cone-shaped base. At this point the gas then reverses its direction and moves up the center of the outer vortex in a vortex core. The separation of the dust occurs during the downward flow of gas when the inertia of the particles forces them out of the gas stream toward the wall of the cyclone. At the bottom of the cone, the particles continue to move downwards because of their momentum in that direction and are collected through a hole at the base of the cone.

The simple cyclone is typically applied to streams up to 50,000 CFM and can obtain 50 percent efficiency on 20-micron particles. Pressure drops of 0.5 to 3 in. of water are typical with gas velocities of 35 to 70 ft per second. Fan horsepower requirements are from 0.12 to 0.74 per 1,000 CFM to recover the lost pressure head.

There are several modifications of the simple cyclone also employed as dust collection equipment. The high efficiency cyclone employs a relatively small diameter and higher gas velocities in order to obtain a greater efficiency. Efficiencies of 80 percent have been obtained on 10-micron particles. Flow rates in this type of cyclone are limited to 12,000 CFM with an increased pressure drop of 3 to 5 in. of water because of the increased gas velocities. The larger pressure drop dictated by this equipment requires a proportionally larger fan horsepower requirement in order to recover the lost pressure head. Another common variation on the simple cyclone is the multiple cyclone in which many small diameter cyclones are employed to treat the same amount of gas as a conventional cyclone. The effect of this approach is to decrease the effective diameter and increase the efficiency. An efficiency of 90 percent is nominal for 7.5-micron particles. The pressure drop and fan horsepower for the multiple cyclone is similar to the high efficiency cyclone.

Impingement Collector.[2189] The impingement collector also uses the higher momentum of the dust particles to separate them from the carrier gas. The dirty gas is accelerated by a venturi and the particle momentum carries the dust particles through a slot in a facing metal plate where they impinge on another plate and are collected. The carrier gas tends to diffuse away from the path of the dust particles. It strikes the first metal plate and is carried away rather than going through the slot. This type of equipment can produce 90 percent efficiency on 10-micron particles with a pressure drop of from 1 to 2 in. of water. Almost unlimited flow rates are handled by impingement equipment with gas velocities of from 50 to 100 ft per second. Fan horsepower requirements for head recovery are from 0.24 to 0.48 per 1,000 CFM.

Dry Dynamic Collector.[2189] The dry dynamic collector is unique in that it uses a specially designed fan to separate the dust particles from the carrier gas and thus has no effective pressure drop. The gas stream is drawn into the collector and accelerated by the impellers of the fan causing the heavy dust particles to be thrown to the outside of the fan chamber. Here they are collected as a concentrated stream and sent to a hopper where they settle out. Since the dynamic collector employs a fan, there is no pressure drop through the equipment and the only utility required for this equipment is the horsepower for the collector itself. The horsepower required for a dynamic collector is slightly greater than that for a fan utilized for the same duty, since the mechanical efficiency is somewhat smaller for the collector. Normally the dynamic collector can handle up to 17,000 CFM of dirty gas with efficiencies of 80 percent on 15-micron particles.

Electrostatic Precipitation[2188]

Electrostatic precipitators use an electrical field for charging the particles in the incoming, pollutant-laden gas causing the charged particles to migrate to a collecting electrode because of the electrical field. Particles are collected on the opposite-polarity electrode and transferred to storage for disposal. Control equipment of this type has had extensive application in many fields of pollution control. A primary advantage of electrostatic precipitators is the relatively low operating costs of these units. Power requirements are low with the gas pressure drop rarely exceeding 1/2 to 1 in. of water. Additional power must, of course, be supplied in the form of electric energy required to ionize and collect the particulate material. The total power requirements for electrostatic precipitator units, however, are low compared with power requirements to attain equivalent efficiencies with other collecting mechanisms; they range between 0.1 and 0.6 kw per 1000 CFM. Electrostatic precipitation units are commonly designed to operate at greater than 90 percent particulate removal efficiencies on particles of 2 microns or less with gas flow rates from 10,000 to 2,000,000 CFM. The initial cost (purchase and installation) of electrostatic precipitation equipment is high relative to initial costs for mechanical collectors or wet scrubbing systems.

Fabric Filtration[2188]

The third class of dry collection equipment which must be considered is fabric filters. In this type of unit, the exhaust gas stream to be treated is passed through a fabric filter bag which collects the particulate material in the exhaust gases while allowing the gases to pass through to the stack for emission. Very large areas of fabric are used to filter gas streams. The pressure drop or resistance to air flow in fabric filter units increases as the dust loading builds up on the fabric. In general, the pressure drop for this type of unit is between 5 and 10 in. of water. Various cleaning mechanisms are used periodically to remove collected particulate material from the fabric filters.

Particulate collection efficiency for this type of unit often exceeds 99.5 percent. Fabric filter units are relatively unaffected by dust loading or gas throughput up to their design capacity. For this reason they represent one of the most positive and efficient particulate control devices available. When used in conjunction with a solid adsorbent substance, fabric filtration can achieve a high degree of gaseous pollutant removal.

Fabric filtration suffers from two major limitations. Humid gas streams cause problems because of caking and binding of the collected particulate material on the fabric surface. This causes greatly increased pressure drop and, in some cases, prevents air flow through the filter installation. The second major limitation is in the cleaning of high temperature exhaust gases. Certain fabric filter materials, such as glass fibers and aromatic polyimide fabrics, have the ability to withstand exhaust gas streams up to 550 F. For gas temperatures above this level, or when it is desirable to use less expensive filtering materials such as nylon, cotton or wool, the gas stream must be cooled prior to entry into the fabric filter unit.

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RADIOACTIVE WASTE SOLIDIFICATION

1. INTRODUCTION

The solidification of liquid radioactive wastes is utilized as a pretreatment for disposal. Solidification results in the conversion of the liquid wastes to solids to provide greater safety during handling, transportation, and disposal. The increased safety associated with the solid wastes compared to the liquid is because the solid form is less mobile, less soluble in water, smaller in volume, and more rugged physically.

Several different processes have been developed for solidifying radioactive wastes. Generally, these processes are broken down into two categories. They are high-level radioactive waste solidification processes, and low- and intermediate-level solidification processes. The high-level solidification processes are used for the solidification of the spent reactor wastes generated from nuclear power plants. The spent reactor fuel is in the solid form when it is removed from the reactor and shipped to a reprocessing plant where it is processed for the recovery of the usable fission materials (i.e., U^{233}, U^{235}, and Pu^{239}) which are refabricated into new fuel elements. The high-level reactor wastes are contained in the aqueous effluent from the reprocessing step. The incentive to recover the reactor spent fuel is two-fold: a need to prevent depletion of the present uranium stocks, and the economic benefits realized which can represent a savings of approximately \$38,000 per metric ton of fuel processed. [0551]

Solvent extraction using nitric acid or nitrate salts is the means currently used for the first-stage removal of the fissionable materials. The resultant high-level wastes are primarily aqueous solutions of inorganic nitrate salts (which will decompose at temperatures below 500 C). Any differences in the waste streams generated will mainly occur due to variations in the amount and type of salts added to the solutions during reprocessing. These variations can have a marked impact on the solidification process conditions and on the nature of the final product.

In the United States four processes have been developed for the solidification of these types of wastes. They are pot calcination, spray solidification, phosphate glass solidification, and fluidized bed calcination. Basically, in each of these four processes, heat is applied to raise the temperature of the waste to drive off the volatile constituents leaving a melt that will eventually cool to a solid. Generally, chemicals are added to the waste stream to reduce the melt below 1,200 C. In all these processes, additional gas and vapor streams are generated which require additional processing. These gaseous wastes can either be filtered and released or recycled. The latter alternative is more attractive and is accommodated more easily and economically if the solidification process is conducted at the same facility as the fuel reprocessing.

The solidification processes for the low- and intermediate-level wastes are adaptable to a number of different types of waste streams. These include waste generated at nuclear power plants and fuel reprocessing facilities, along with the wastes resulting from research laboratories and medical and industrial applications of radioisotopes. The wastes generated at nuclear power plants include radioactive filter sludges, spent resins, and chemical wastes which result from the treatment of the condensate water and water from other sources in the plant. The majority of the low- and intermediate-level waste streams are generated during the reprocessing of the spent reactor fuel. The intermediate-level wastes are obtained from evaporating second- and third-cycle wastes, cell and equipment decontamination, solvent cleanup, and off-gas scrubbers. The volume of these wastes range from 200 to 500 gallons per metric ton of fuel processed. These wastes are principally nitrate solutions of sodium, potassium, aluminum, and iron, and often contain sulfate, fluoride, and phosphate in addition. Their activity levels are generally less than a tenth of a curie per gallon. The low-level wastes from fuel reprocessing plants contain only very small amounts of inert chemicals and radionuclides. These wastes are very large in volume. Evaporator condensates alone may average 10,000 gal per metric ton of fuel processed.[0705] These wastes are generally released to the environment even though there is a trend toward decontaminating these wastes and solidifying the resulting mixture.

Three solidification processes for the low and intermediate wastes will be considered in this report. These processes include the incorporation of wastes in asphalt, cement, and polyethylene.

2. OPERATION PRINCIPLE

Solidification of radioactive wastes is based on the principle of converting the wastes from a mobile aqueous state to a solid state to reduce the mobility of radionuclides after burial or storage. The process for the solidification of the high-level radioactive wastes is based on the addition of heat to volatilize the waste, leaving a melt that will eventually cool to a solid. To lower the waste melt temperature and to enhance the solidified product, chemical modification of the waste composition is required. Generally, compositions for waste solidification require the addition of at least 70 mole percent of inert chemicals to incorporate the wastes into a low temperature melt (less than 1,000 C). The solidification processes for low and intermediate wastes depends on the immobilization of the wastes by the incorporation of relatively inert solid materials to form a solid product. In several of the processes excess water is removed by heating the wastes until the water is volatilized.

3. PROCESS DESIGN

This section is divided into two parts. In the first part the desired characteristics of the solidified waste product are developed. These characteristics are of primary importance in evaluating the adequacy of the solidification processes. In the second part the design of the solidification processes for the high-level and low- and intermediate-level wastes is described.

Solidified Waste Characteristics

The purpose of any solidification process is to achieve a substantial increase in the safety associated with the storing, transportation, and disposal of radioactive wastes. The increase in the safety of the solidified waste is a result of the reduction in the mobility of the radionuclides contained in the waste. To assess the safety of any disposal technique it must be recognized that solidification is only part of the total disposal scheme. The other important considerations are the type of container used to hold the solidified waste and the type of disposal method utilized.

The basic criterion for any solidification process is to prevent radioactivity beyond safe limits from entering the human environment. These safety limits are usually defined in terms of the radionuclide's Maximum Permissible Concentration (MPC) in air and water. For reference purposes, the acceptable concentrations for exposure to the general population are one-third the concentrations listed in the Code of Federal Regulations in (10CFR20).[2149] These limits correspond to a whole body exposure level of 170 mrem per year. The present Atomic Energy Commission (AEC) regulations further require that the radioactivity be kept as low as possible and have established a limit of 5 mrem per year for nuclear power plants. This latter limit is desirable and probably should be used in assessing the adequacy of any disposal process including the waste solidification processes. To achieve these limits the desired characteristics of the solidified waste are presented below.

Dispersibility. The physical properties of the waste, such as hardness and brittleness, determine its dispersibility. In the event the waste container is breached, the physical ruggedness of the solidified waste will determine its tendency to be dispersed. A brittle or easily scattered waste will result in a greater contamination to the environment than a physically rugged waste. The solidified waste and its container should be designed to withstand the specified accident conditions during transportation [0562] and also be able to withstand all accident conditions during storage.

Leachability. A low leachability of the solidified waste is required to minimize the release of radioactivity to the environment in the event that the waste container is breached and water should come in contact with the solidified waste. The ideal leach rate of the solidified waste can be assessed in terms of the specific activity of the radionuclides present and their MPC values in water. [2149] The ideal leach rate is determined as follows:

$$L.\ R. = \frac{(MPC)}{(S.A.)} \cdot \left(\frac{V}{T}\right) \cdot \left(\frac{1}{A}\right)$$

where

L.R. = leach rate, gm/cm^2 - day
MPC = maximum permissible concentration of radionuclide in water, $curies/cm^3$
S.A. = specific activity of radionuclide, curies/gm
V = volume of water contacted, cm^3
T = time of contact, days
A = area of waste contacted, cm^2

To provide an indication of the ideal leach rate assume one square centimeter of solidified waste were contacted by one thousand cubic centimeters of water for one minute. This is equivalent to a flowrate of 0.264 gallons per minute. For a waste containing only Sr^{90} with a specific activity of 142 curies/gm and a 168 hour MPC value of 1×10^{-12} $curies/cm^3$ the leach rate of the solidified waste should not exceed 1×10^{-8} gm/cm^2 - day. Since the ideal leach rate is a function of specific activity, which decreases with time, the maximum allowable leach rate would increase with time.

Stability. The stability of the solidified waste is important to assure that the basic structure and properties of the waste remain intact. The basic structure and chemical properties of the waste will change due to the decay of the radioactive materials to other chemical elements. This effect is especially pronounced for reactor produced waste since approximately 30 percent of the fission products present after 6 months out of the reactor will eventually decay to other chemical elements. Since the change in the chemical composition of the waste is impossible to prevent, the wastes should be held a sufficient time before solidification to allow a majority of the short-lived isotopes to completely decay. The exact time the waste should be held before solidification is a function of the half-life of the radionuclides present and should be such that any changes in the solidified waste composition will not affect its basic structure or physical properties.

The exposure of the wastes to high levels of radiation can cause radioactive gas evolution, swelling and discoloration of the waste, and changes in its leach rate and physical properties. The exposure rate and its effect on the solidified waste are dependent upon the type of waste and amount of radioactive material contained. The level of radiation damage is usually determined experimentally. Once the level of damage is determined the amount of radioactivity or the amount of radioactive material contained in the waste should be kept below the level at which significant damage occurs.

The temperature stability of the waste determines the maximum temperature at which the waste can be exposed before the gas formation and dispersion occurs. Generally, gas formation from solidified wastes is not significant if the waste temperature does not approach processing temperature.[0715] For some of the high-level solidification processes, a few exceptions have been indicated for calcine from feeds with high sodium nitrate content (nitrogen oxide volatility) and for some phosphate-sulfate melts (sulfur oxide volatility).[0715]

Thermal Conductivity. The maximum temperature of the solidified waste must be maintained below prescribed limits to prevent the waste from melting or vaporizing. To achieve these limits, a high thermal conductivity is required to minimize the temperature rise between the center and outer surface of the wastes. The temperature difference between the center and outer surface of a solid cylinder of self-generating heat varies as:

$$\Delta T \propto \frac{1}{K} \cdot Q \cdot D^2$$

where ΔT = temperature difference
K = thermal conductivity
Q = heat rate per unit volume
D = diameter of cylinder

Thus, a higher thermal conductivity will linearly decrease the temperature at the center of the waste and increase the amount of self-generating heat that can be included in the waste. By increasing the amount of self-generating heat the storage time before solidification is decreased. In addition, a higher thermal conductivity also increases the size of the storage container and allows for a decrease in the specific volume (liters/gram) of the solidified waste.

Corrosiveness. Corrosiveness of the waste determines the life of its container. This is very important for as long as the container remains intact the leach rate and dispersibility of the waste is held to a minimum. Most solidified wastes are stored in carbon or stainless steel containers. Even though these containers are adequate for the short term, the long-term effects of corrosion have not been adequately evaluated. At the present time studies are being conducted especially for the high-level solidified wastes to determine container life.

Process Description

High-Level Solidification Processes. Four processes have been developed for the solidification of high-level wastes. They are pot calcination, spray solidification, phosphate glass solidification, and fluidized bed calcination. The pot, spray, and phosphate glass processes have been demonstrated on a full scale, engineering level by Battelle-Northwest at Richland, Washington.[0715, 0716, 0717, 0527, 0732] The fluidized bed process has been demonstrated in a large capacity plant[0694, 0711] by Idaho Nuclear Corporation at Idaho Falls, Idaho. A description of each solidification process is attached (Figures 1 and 2) and basically, in each of these four processes, heat is applied to raise the temperature of the waste to drive off the volatile constituents leaving a melt that will eventually cool to a solid. Generally, chemicals are added to the waste stream to: (1) reduce the melt temperature; (2) prevent the release of volatile components; and (3) improve the properties of the final product.

Each of these processes generate additional gas and vapor streams which contain reduced but still toxic levels of radioactivity. To treat these waste streams for the removal of radioactivity additional auxiliary processing equipment is required. The auxiliary processing system usually includes several separate cycles of evaporation plus condensation followed by a stage of filtration. An acid fractionator is also employed for the removal of nitric acid. This system is followed by a caustic scrubber and further stages of filtration. Decontamination factors of 10^9 have been obtained with liquid effluents.[0716]

The overall characteristics of the four types of solidified wastes are summarized (Table 1) and a brief description of the design of each process is presented below.

Pot Calcination. A batch process in which the processing vessel is also the final container for the solidified waste. In this process the liquid waste is added to the pot and heated in a multiple-zone furnace.

As the waste is heated, scale forms on the wall of the pot. The scale grows in thickness until all the waste in the pot has been calcinated and reaches a temperature of 850 to 900 C. The pot is then cooled, sealed, and taken to storage. The only major requirement for additives to the liquid waste stream is for the retention of the volatile components. The overall cycle capacity with a 12-inch-diameter pot is 14 liters/hr which represents an equivalent waste processing capacity of 0.90 tonnes/day.

The basic elements required for the design of the equipment in pot calcination are: a multiple-zone furnace for heating and cooling, a pot for calcinating the waste, and an off-gas line from the pot that can be continuously washed down. The multiple-zone furnace must be designed to provide different heating regions along the vertical portion of the pot. Six zones for a pot filled with 6 ft of calcine have been found to be adequate.[0715] The pots are made of corrosion resistant material to survive the severe corrosion conditions during processing. Three-hundred-series stainless steel, generally 304L or 310, has been found to be adequate.[0716] Continuous washing of the off-gas line from the pot is required to prevent plugging by entrained calcine or sludge. The continuous washing can be accomplished by condensing the vapors formed in the line.

A major problem in the design of the pot calcination process is retention of volatile components such as sulfate, ruthenium, and mercury. Sulfate can be retained almost entirely in the calcine form[0716] by adjusting the ratio:

$$\frac{\text{Chem. equiv. (alkali + alkaline earth metals)}}{\text{Chem. equiv. (nonvolatile anions)}} \geq 1.1$$

Chemial additives to meet this ratio are usually calcium or sodium nitrates. Since the above ratio also includes potentially volatile alkali metal oxides, the following ratio should also be met:

$$\frac{\text{Chem. equiv. alkali metals}}{\text{Chem. equiv. (nonvolatile anions)}} \le 1$$

The volatilization of ruthenium can be decreased by the addition of phosphate or hypophosphate ions as phosphorous acid. The retention of mercury is difficult since it forms no compounds that are stable at temperatures greater than 600 C. The mercury should be removed prior to solidification by passing the waste through beds packed with copper or aluminum. The copper beds are not feasible if the acid concentration of the waste is greater than 0.5 M.

Spray Solidification. A continuous process in which the liquid waste is fed through an atomizing nozzle into a heated calcine tower. The waste is evaporated, dried, and calcinated to a powder as it falls through the calciner tower. It then falls into a melter where it is melted at temperatures of 800 C to 1200 C. The melt in the melter flows through an overflow weir to a storage pot which is then cooled and sealed. Process gases flow into the adjacent filter chamber where the calcinated powder collects as dust on the porous metal filters. This dust is periodically blown off by sudden pulses of high pressure steam or air and falls back into the melter with the main powder stream. The overall cycle capacity is approximately 20 liters/hr of liquid.

The basic elements required for the design of the equipment in spray solidification are: an atomizing nozzle; a multiple-zone furnace; an off-gas cleaning system; a continuous melter and furnace; and a receiver pot and multiple-zone furnace. The atomizing nozzle is designed to break the feed up into small droplets (80 to 100 microns diameter) to permit drying and calcinating of the feed. Commercial internal-mixing nozzles have proved satisfactory.[0725] The multiple zone heater in the spray calcinator is designed to maintain the temperature in the spray tower higher than the walls of the spray tower to prevent sticking to the tower walls. The calcine dust in the off-gases can be separated by porous stainless steel filters with an average pore size of 65 microns and a total area of 1 sq ft/(liter) (hr) of feed to the calcinater.[0725] The continuous melter which is positioned below the calcinater to collect the powder must withstand the effects of corrosion and high temperature (up to 1,200 C). Platinum is the only known reliable material for the melter at the present time. Other materials such as a chromium-alumina cermet and an alloy of 50 percent chromium-50 percent nickel are being examined. The receiver pot and multiple zone furnace designs are similar to those in pot calcination.

In spray solidification the feed composition has a strong effect on its performance. Additives are required so that a melt-forming matrix which is stable at high temperatures is formed. Phosphate is generally used as the melt former. The melt temperature limits are adjusted using a phosphate flux with an overall cation-to-phosphate ration (M/P) of 2 to 3.[0725] In this relationship, M is the total metal ion equivalent and P is the total molarity of phosphorous present. The melt temperature increases with the M/P ratio approaching 1,000 C at a M/P ratio of 3.

Sulfate and ruthenium are the two principal products most easily volatized. The sulfate is retained in the melt by the addition of calcium which combines chemically with the sulfate. The ruthenium volatility is reduced by the elimination of the melt-making flux from the feed and the addition of all the melt-making flux to the melter.

Phosphate Glass Solidification. A continuous glass solidification process which is carried out in three steps: feed preparation; low temperature denitration-evaporation; and high temperature glass forming. The feed preparation involves the addition of glass-forming chemicals to the liquid waste. The liquid waste which contains all the melt-making additives is first fed to an evaporator where it is concentrated into a thick phosphate slurry. This slurry is fed to a continuous melter where the material is heated to 1,000 to 1,200 C to form a molten glass. The molten glass then flows into a storage pot which is cooled and sealed. The process capacity is limited by the melter which has a capacity of 10 to 12 liters/hr compared to the evaporator capacity of 35 liters/hr.[0718]

The basic elements required for the design of the equipment are: a continuous denitrator-evaporator; a melter feed system; a continuous melter and furnace; and a receiver pot and multiple zone furnace. The evaporator design must be capable of handling corrosive liquids, providing low hold-up volume and maximum suspension of solids. The evaporator is made of titanium and is constructed of a special design.[0732] The melter feed system is designed to pump and meter the waste flow between the evaporator and the melter. Special designs using either an airlift or slurry pump have been developed. The melter requirements are the same as those for the spray solidifier except that the heat transfer requirements are 50 to 100 percent higher. The receiver pot design is similar to that for pot solidification.

The chemical additives are added directly to the feed and consist mainly of orthophosphoric acid. To form a good quality glass, one mole of phosphate is required per mole equivalent of nonvolatile cation.[0732] If the ratio is less than one, a poor grade glass is formed and, if greater than one, the excess phosphate is evolved until the ratio is about one. If the mole percent of oxides of the alkali metals is less than half the total metal oxides in the melt, additional alkali metals (i.e., sodium nitrate) must be added to obtain a glass that forms at 850 to 1,000 C and has good handling properties.

In the evaporator about 0.5 to 1 percent of the ruthenium will volatilize but no appreciable sulfate or phosphate volatilization has occurred.[0716] In the melter the principal off-gases are water, nitrates, sulfate (when present in waste), and ruthenium. When sulfate is not present the off-gases from the melter are combined with the off-gases from the evaporator, or condensed separately and recycled to the evaporator to reduce the overall off-gas activity. When sulfate is present, steam additions are required to help recover the sulfate and to prevent corrosion by diluting the condensate and reducing its temperature.

Fluidized Bed Calcination. A continuous process in which the liquid waste is converted to granular solids by heating in a fludized bed of the granular solids. In this process the liquid waste is injected through an atomizing nozzle into the side of a heated bed (400 to 600 C) of granular solids. The bed is continuously fluidized by gas flowing upward through the bed. As the waste contacts the hot bed it is evaporated and calcinated as coatings of the bed particles. The bed particles are continuously removed from the calcinator and transported to storage bins. The calcine that is entrained with the process gases is removed from the gas stream by cyclone separators or filters and transported to the storage bins. About 60 percent of the solidified waste product is removed from calciner and the remainder is removed during the processing of the off-gas stream. The overall cycle capacity is 180 to 260 liters/hour.

The basic elements required for the design of the equipment in the fluidized bed process are: an atomizing nozzle; a calcinator and furnace; and an off-gas cleaning system to remove the calcine dust. The atomizing nozzle is designed to break up the feed into small droplets to permit rapid drying without caking. Commercial external-mixing pneumatic nozzles are used with a gas volume of 500 to 800 times the volume of the liquid feed.[0694] Air or superheated steam is used for atomization. The calcinator size is 3 to 6 times the hourly volume of liquid feed to the calcinator and has a length to diameter ratio in the range of 1.5:1 to 4:1.[0715] The heat requirements for the calcinator is one kilowatt for each liter per hour of liquid feed. The heat is provided by an in-bed heat exchanger through which sodium-potassium (NaK) circulates. The sodium is heated externally to about 740 C and circulated by an electromagnetic pump. The calcine dust in the off-gas stream is removed by the use of cyclones and porous stainless steel filters with periodic pulse blowback for on-line cleaning. The pulse blowback system is similar to the system used in spray solidification.

Additives to the feed solution are primarily required to retain the volatile components and not to enhance the final solidified waste product. Ruthenium volatility is reduced to about 1 percent when sugar is added to the feed. [0715] Sulfate and fluoride is retained with the calcine (99%) and fluoride corrosion is controlled by the addition of calcium in stoichiometric equivalence to the amount of fluoride present. [0715]

Low and Intermediate Solidification Processes. Solidification processes have been developed for the incorporation of low and intermediate wastes in asphalt, cement, and polyethylene. These treatment processes are fully described elsewhere [0547,0697, 0704,1017,] and will only be briefly described here. The treatment processes for each of the solidification processes is similar. The waste and the solidification material are added and mixed together in a predetermined ratio. This ratio depends on the type of waste involved. Studies have defined compositions of asphalt and polyethylene for incorporation in organic and inorganic waste streams. [0547] These compositions are attached (Table 2). Tests have resulted in a ternary operating diagram for the incorporation of filter sludge and ion exchange resins in cement.[0697] These results are also attached (Figure 3).

The solidification process for asphalt and polyethylene consists of adding the waste to the asphalt or polyethylene in an evaporator with a wall temperature between 130 and 160 C. Mixing is accomplished by agitator paddles. The paddles turn with a downward forcing action that forces the mixture out the bottom and into the disposal container. In the solidification process for cement the waste and cement are generally mixed directly together in 55-gal drums.

4. PROCESS ECONOMICS

For the four high-level solidification processes only cost studies for pot calcination were found to be available. [0705] These cost studies were made using an economic model based on a discounted cash flow technique. This type of model requires that the income received must provide for the recovery of the investment by the establishment of a reserve account to pay all waste management operations that remain to be completed after all income has ceased. Using this model the costs of pot calcination were calculated as a function of the age of the waste and size of the storage container. These costs are presented for the case in which the center-line temperature of the waste is held at less than 900 C when standing in air (Figure 4). These costs ranged from $4,200/metric ton of fuel for 1-year-old waste in 6-in.-diameter pots, to $460/metric ton of fuel for 30-year-old waste in 24-in.-diameter pots.

Cost estimates for the incorporation of aqueous intermediate-level waste in asphalt and polyethylene have been made.[0547] These cost estimates were made using a price of $0.015/lb for asphalt and $0.20/lb for polyethylene. The total processing cost was $0.80/gal of waste for asphalt and $0.34/gal of waste for polyethylene.

5. PROCESS APPLICABILITY

The high-level solidification processes have been developed especially for the spent reactor wastes generated from nuclear power plants. These wastes include the reactor-produced fission products as well as the actinides or transuranium elements. In addition to the spent reactor wastes, these processes are applicable to all high-level radioactive wastes (wastes that contain concentrations of radioactivity greater than 0.4 curies per gallon) or to wastes that present special disposal problems such as the actinides or the transuranium elements.

Since these solidification processes result in a waste volume reduction their applicability to certain types of wastes can be limited by the waste heat generation rates. This is a problem not only for the wastes generated by the presently constructed thermal power reactors, but the size of this problem will increase with the introduction of the fast breeder reactors. To assess the magnitude of this problem calculations were made to determine the maximum allowable heat that would be stored in a particular storage container for each of the four solidification processes. The reactor-produced fission product heat generation rates are shown as a function of time for both the current thermal power reactors and the proposed fast breeder reactors (Figure 5). As noted, the fast reactor heat generation rates are approximately five to ten times higher than those of the current thermal power reactors.

The maximum container heat content was calculated assuming a maximum waste temperature of 900 C and a storage environment of 20 C air, which corresponds to a container wall temperature of approximately 450 C. For these conditions, the heat content of a cylindrical storage container is shown as a function of container diameter and waste thermal conductivity (Figure 6). Combining this data with that previously shown (Figure 5) the maximum heat content and corresponding age of the fission products (storage time before solidification) was determined for each of the four solidification processes. This data is presented for a 6-inch-diameter container (Table 3). For the present thermal power reactors the required age of the fission products or the storage time before solidification varied from 0.2 to 2.1 years and for the fast reactors from 2.7 to 9.5 years. For an 8-inch-diameter container the required age for the fast reactor would vary from 8.4 to greater than 10 years. This data was presented for storage in air and the age or storage time of the waste would be reduced if the containers were stored in water or in an enclosed, air-conditioned room. This data indicates that the waste heat content can limit the use of these solidification processes especially with the fast breeder reactor wastes. To overcome this problem several of the more active fission products such as Sr^{90}, Ru^{106}, Cs^{137}, and Ce^{144} may have to be removed from the waste prior to solidification.

A comparison of the four solidification processes is presented (Table 4). From the standpoint of process and flexibility, pot calcination is superior to the other three processes, but the other three processes are superior in terms of the solidified waste product. A comparison of the characteristics of the solidified waste products for each process shows that spray solidification comes closer to matching the desired characteristics of the solidified waste developed in Section 3. It must be recognized that solidification is only part of the total disposal scheme and that the final comparison or selection must be made in conjunction with the disposal method to be utilized.

The low and intermediate solidification processes are applicable to those wastes that contain concentrates of radioactivity less than 0.4 curies per gallon and are disposed of by direct burial in the ground. These solidification processes are not applicable to all waste streams with concentrates less than 0.4 curies per gallon, since it would not be acceptable to dispose of materials such as the actinides in these concentrations by solidification and burial directly into the ground. In general, these solidification processes are more adaptable to the short-lived isotopes (6 months to 30 years) and less hazardous materials. The source of these types of wastes are the secondary streams generated at nuclear power plants and fuel reprocessing facilities, along with the wastes resulting from research laboratories and medical and industrial applications of radioisotopes.

Cement, asphalt, and polyethylene are used for the solidification of these types of wastes. Cement products are only moderately insoluble compared to the asphalt and polyethylene products. The leach rates of asphalt and polyethylene products are 50 to 100 times lower than those of cement products containing similar amounts of waste salt. A comparison between a good asphalt product (about 60 Wt. % salts) and a good cement product (about 25 Wt. % salts) shows that the weight percent of Cs^{137} leached in 10 weeks from the cement product was 58 percent and from the asphalt product was 0.56 percent.

Cement can be used with almost all waste streams but the products formed are inferior to the asphalt and polyethylene products in terms of solubility. The integrity of the cement product also decreases greatly as the concentration of soluble salts increases.[1017] When low concentrations of waste salts are used, the volume of the final cement product is much larger (60%) than the original waste volume. With asphalt products volume reductions of almost two have been obtained.[0697] In addition, most operations with cement are dusty and cumbersome and good mixing is difficult to achieve.

In general, asphalt and polyethylene are better materials than cement for solidifying low and intermediate wastes except for waste streams that contain significant amounts of oxidizing agents. Economically, asphalt is preferred to polyethylene since its processing costs are less. Asphalt is not recommended for wastes that contain oxidizing salts since tests[0547] have shown that mixtures containing relatively large amounts of nitrate or nitrite burn vigorously and that a mixture containing 65.6 Wt. percent nitrate (90 Wt. % $NaNO_3$) with a porosity of approximately 50 percent can be detonated with blasting gelatin. Polyethylene can probably be used with oxidizing salts, but further studies are needed to assess the safety of the system. For organic wastes polyethylene is recommended since a high percentage of the wastes can be accommodated without the use of an inert filter that is required with the asphalt-organic mixture.

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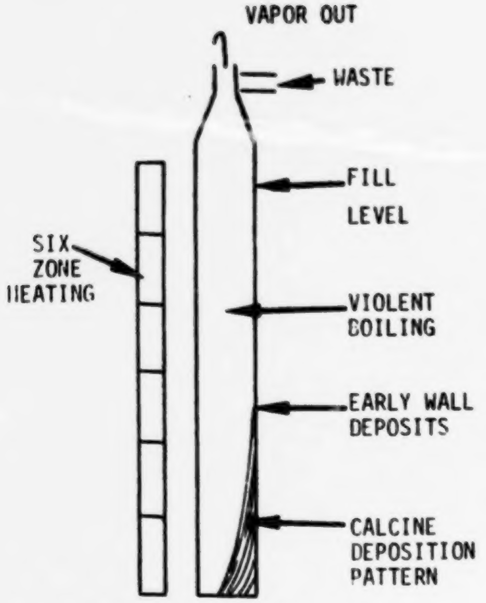
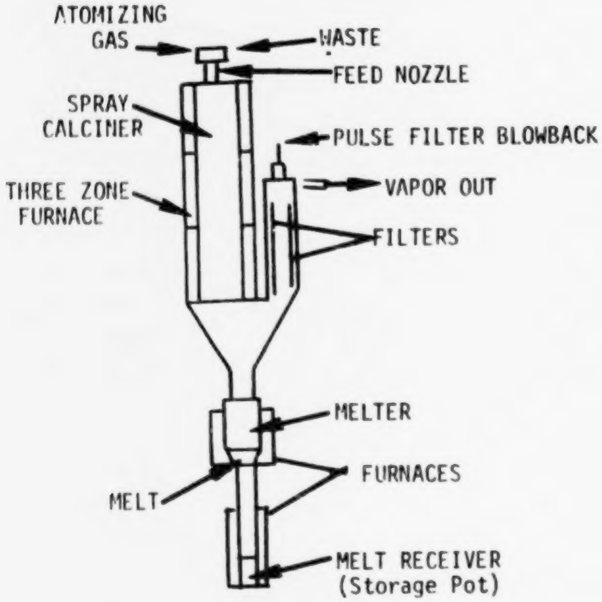
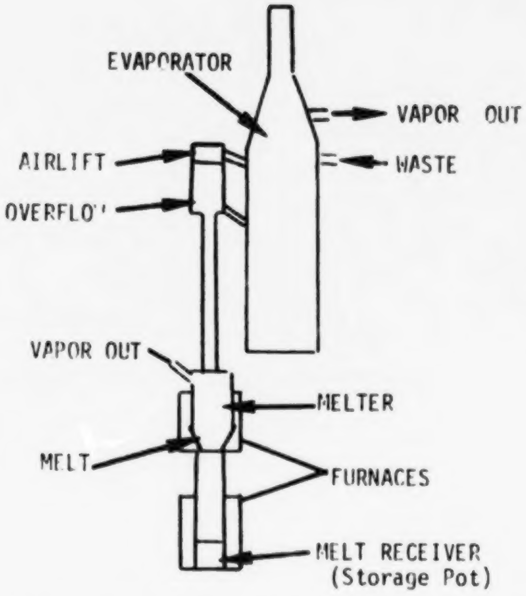


POT CALCINATION PROCESS

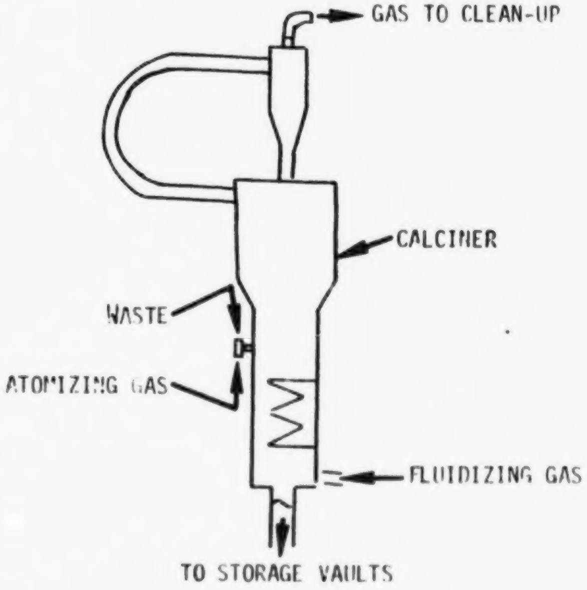


SPRAY SOLIDIFICATION PROCESS

Figure 1. Pot Calcination and Spray Solidification.



PHOSPHATE GLASS SOLIDIFICATION



FLUIDIZED BED CALCINATION

Figure 2. Phosphate Glass Solidification and Fluidized Bed Calcination.

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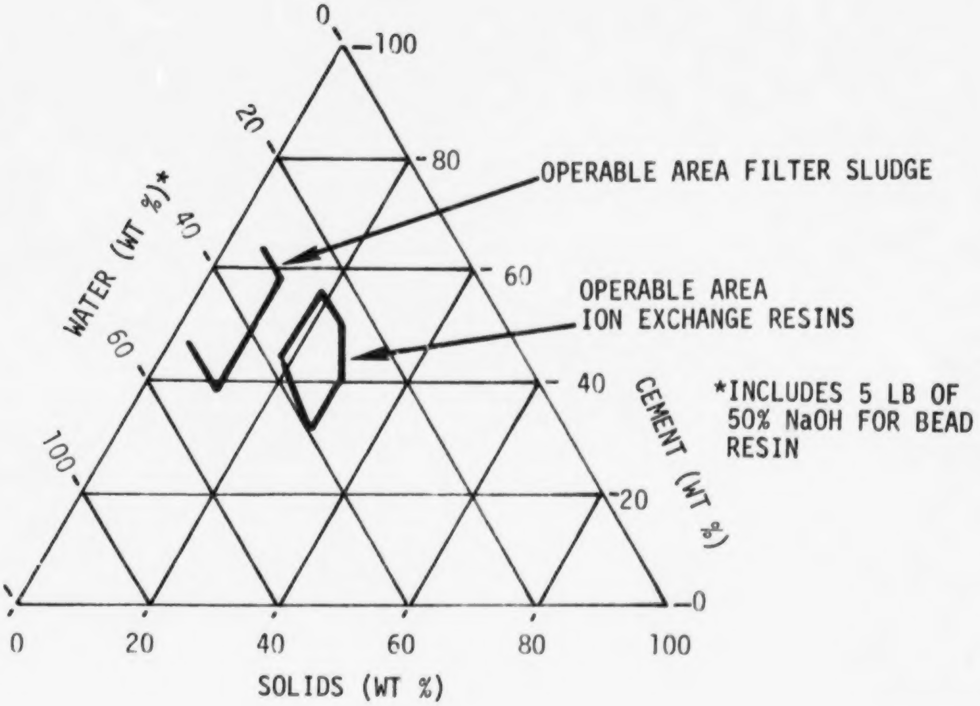

Figure 3. Cement Solidification Process Ternary Operating Diagram for Filter Sludge and Ion Exchange Resin Wastes.

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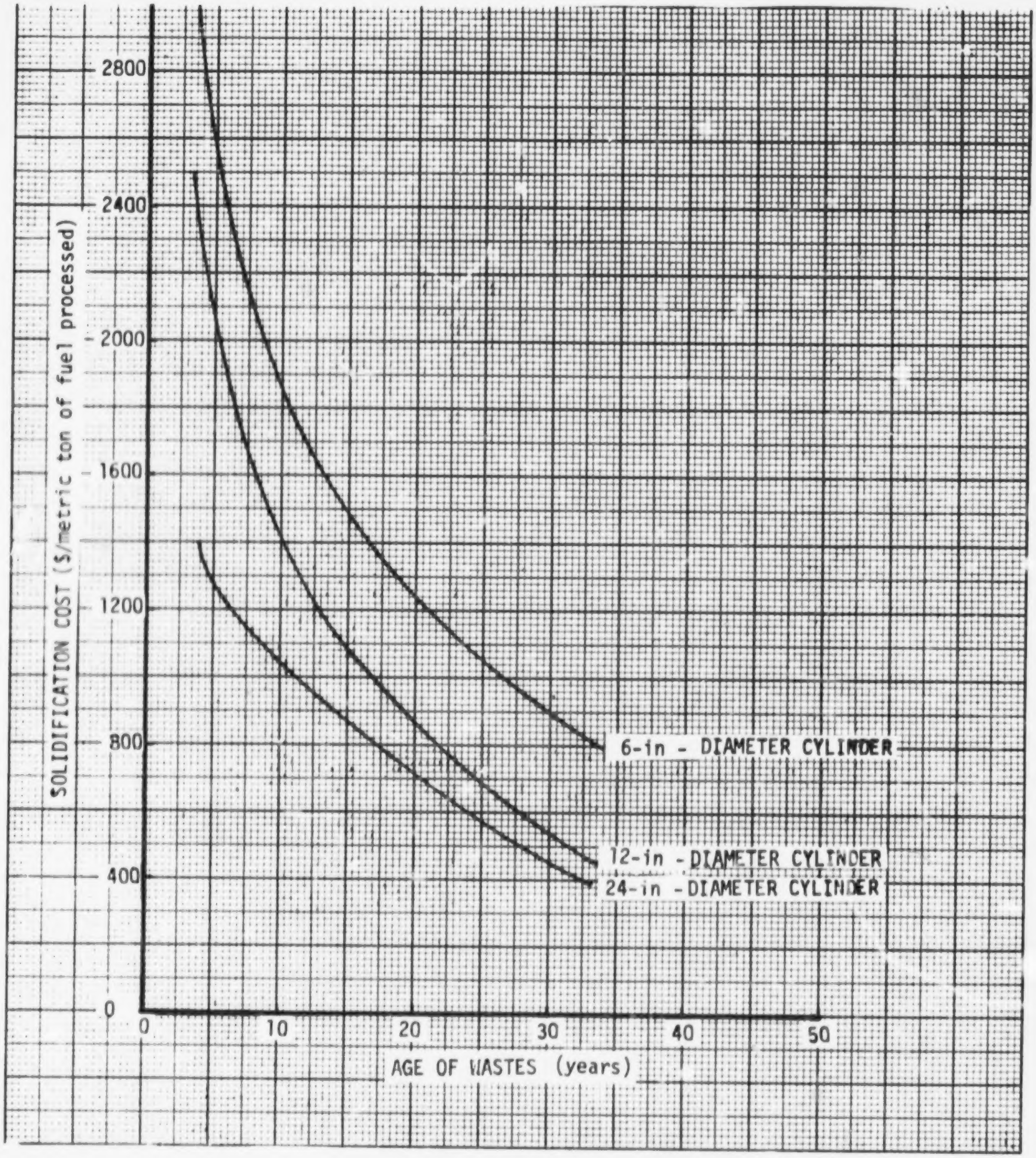

Figure 4. Pot Calcination Costs as a Function of the Age of the Waste. (0705)

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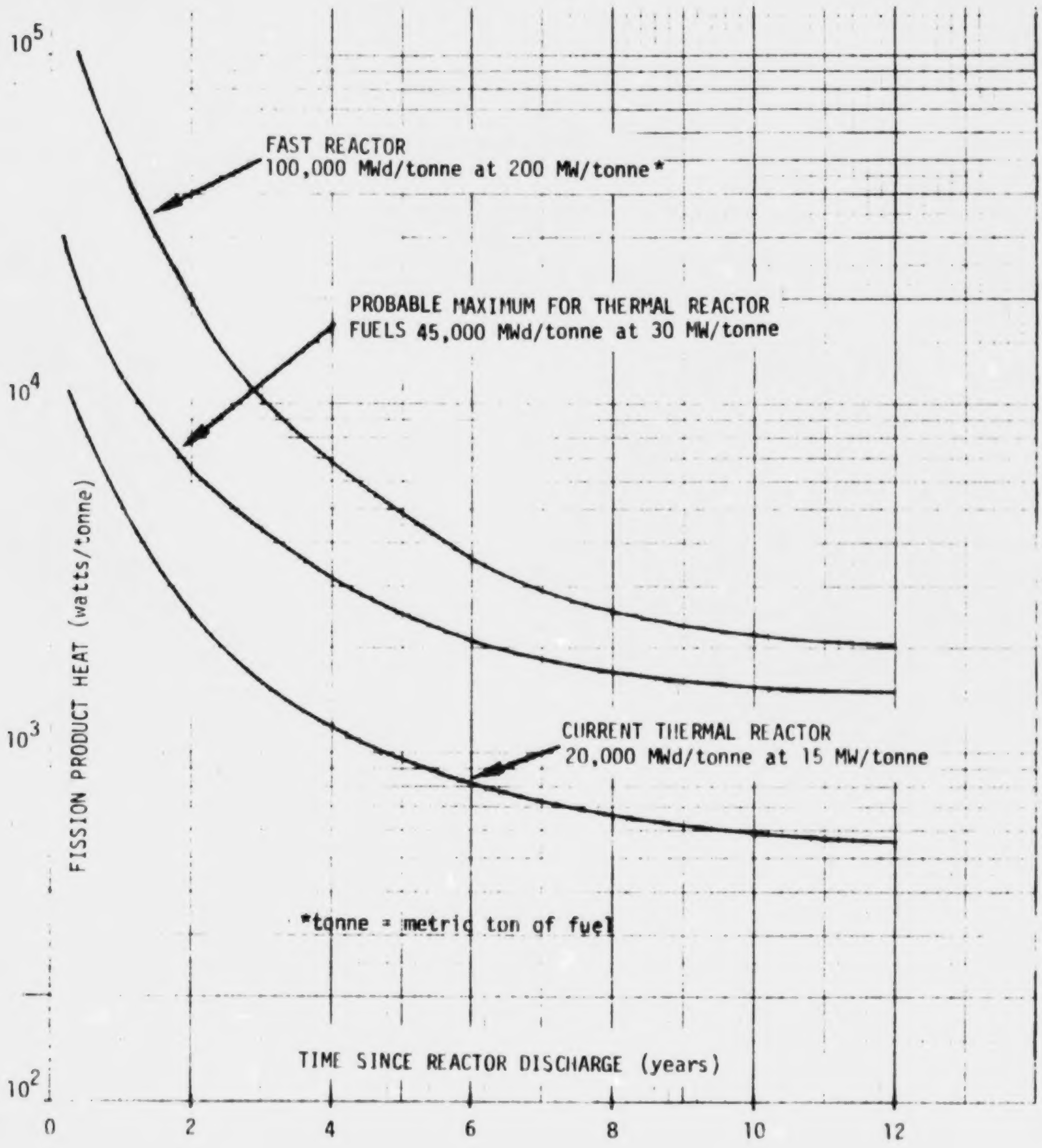

Figure 5. Fission Product Heat Generation Rates. (0716)

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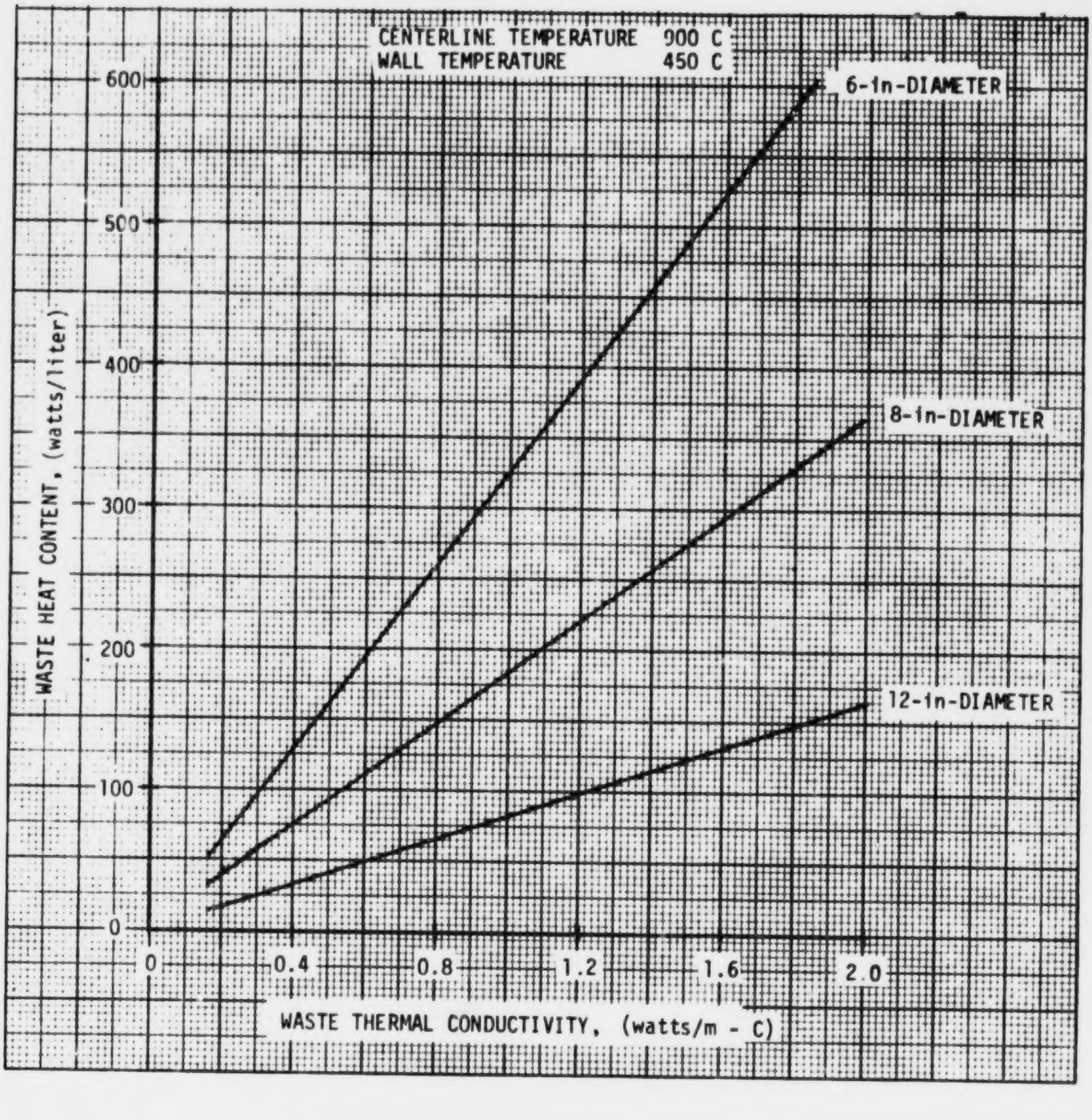

Figure 6. Waste Heat Content as a Function of Waste Thermal Conductivity and Pot Diameter.

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TABLE 1

CHARACTERISTICS OF HIGH LEVEL SOLIDIFIED WASTE (0705)

	Pot Calcination	Spray Solidification	Phosphate Glass	Fluidized Bed
Form	Calcine Cake	Monolithic	Monolithic	Granular
Description	Scale	Microcrystalline	Glass	Amorphous
Hardness	Soft	Hard	Very hard	Moderate
Friability	Crumbly	Tough	Brittle	Moderate
Bulk Density, g/mℓ	1.1 to 1.5	2.7 to 3.3	2.7 to 3.0	1.0 to 1.7
Thermal Conductivity, watts/ m- C	.19 to .26	.87 to 1.73	.69 to 1.73	.17 to .43
Leachability, g/cm^2-day	10^{-1} to 1	10^{-6} to 10^{-3}	10^{-7} to 10^{-4}	10^{-1} to 1
Volume, liters/1000 MWd (thermal)	1. to 2.5	1.2 to 3	1.5 to 5	1.5 to 5
Chemical Composition, mole %				
Fission product oxides	15 to 80	5 to 30	5 to 25	5 to 50
Inert metal oxides	10 to 50	40 to 50	10 to 30	10 to 90
Phosphorous oxides	∼0	25 to 40	∼60	∼0
Maximum Stable Temperature, C	∼900	Phase separation at 900	Devitrifies at ∼500	∼600
Container Material	Stainless Steel	Mild or Stainless Steel	Mild or Stainless Steel	Mild or Stainless Steel

TABLE 2

ASPHALT AND POLYETHYLENE MATRIX COMPOSITION FOR ORGANIC AND INORGANIC WASTES (0547)

Composition, wt%			Comments on Product	
Waste	Matrix Material	Filler	At 160 C	At 25 C
Organic				
25 (tributyl phosphate)	38 (asphalt)	37 (Attapulgite-150)[a]	Pours	Firm, but bleeds
25 (tributyl phosphate)	35 (asphalt)	40 (Grundite)[b]	Pours	Soft and tacky
25 (tributyl phosphate)	37 (asphalt)	38 (Attacote)[c]	Pours	Firm, but bleeds
25 (tributyl phosphate)	37 (asphalt)	38 (Attaclay)[d]	Pours	Soft and tacky
30 (tributyl phosphate)	70 (DYLT polyethylene)	None	Fluid	Very good
30 (tributyl phosphate)	70 (DYDT polyethylene)	None	Very fluid	Good
30 (carbon tetrachloride)	70 (DYDT polyethylene)	None	Very fluid	Good
30 (tetrachloroethylene)	70 (DYDT polyethylene)	None	Very fluid	Good
Inorganic				
40 ($NaBO_2$)	60 (asphalt)	None	Very fluid	Good
60 ($NaBO_2$)	40 (asphalt)	None	Very fluid	Good
50 [$Ca(BO_2)_2$]	50 (asphalt)	None	Fluid	Good
55 [$Ca(BO_2)_2$]	45 (asphalt)	None	Fluid	Good
20 ($NaBO_2$)	80 (DYLT polyethylene)	None	Fluid	Good
30 ($NaBO_2$)	70 (DYLT polyethylene)	None	Fluid	Good
40 ($NaBO_2$)	60 (DYLT polyethylene)	None	Fluid	Good
20 ($NaBO_2$)	80 (DYDT polyethylene)	None	Very fluid	Good
40 ($NaBO_2$)	60 (DYDT polyethylene)	None	Very fluid	Good

[a] Attapulgite-150: a magnesium aluminum silicate drilling clay produced by Minerals and Chemicals Philipp Corp.
[b] Grundite: a high-strength bonding clay produced by the Illinois Clay Products Co.
[c] Attacote: a magnesium aluminum silicate coating clay produced by Minerals and Chemicals Philipp Corp.
[d] Attaclay: a magnesium aluminum clay produced by Minerals and Chemicals Philipp Corp.

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TABLE 3

ALLOWABLE HEAT CONTENT OF HIGH-LEVEL SOLIDIFIED WASTE

	Pot Calcination	Spray Solidification	Phosphate Glass	Fluidized Bed
Thermal Conductivity, watts/m- C				
Range	.19 to .26	.87 to 1.73	.69 to 1.73	.17 to .43
Average	.23	1.30	1.21	.30
Maximum Heat Content (6" Dia. Pot)				
Watts/liter	75	425	395	100
*Watts/metric ton of fuel	2250	12,750	11,850	3000
Age of Fission Products, years				
Current Thermal Reactor	2.1	.2	.2	1.7
Maximum Thermal Reactor	5.5	1.0	1.0	4.2
Fast Reactor	9.5	2.7	2.8	6.9

*Solidified Waste Volume = 30 liters/tonne

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TABLE 4

COMPARISON OF POT, SPRAY, PHOSPHATE GLASS, AND FLUIDIZED BED SOLIDIFICATION PROCESSES

	Pot Calcination		Spray Solidification		Phosphate Glass Solidification		Fluidized Bed Calcination	
	Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages	Advantages	Disadvantages
1. System	Simple			Complex		Complex		Complex
2. Type		Batch	Continuous		Continuous		Continuous	
3. Amenability to Scale Up		Limited	Good		Good		Fair	
4. Flexibility for Waste Variations	Minimum			Moderate		Moderate		Moderate
5. Specific Restrictions	None			Requires Platinum Melter Requires Good Waste Flow Control High Ruthenium Volatilization		Requires Platinum Melter Requires Good Concentrate Flow Control Does Not Retain Sulfate in Solid		Requires Complex Heating Scheme Amount of Self-Generating Heat Limited
6. Product		High	Low		Lowest			High
7. Product Thermal Conductivity		Low	Highest		High			Low
8. Product Toughness		Soft	Tough			Brittle	Moderate	

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APPENDIX B - PROFILE REPORTS

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PROFILE REPORT ON
CADMIUM AND CADMIUM COMPOUNDS

Cadmium Oxide (81), Cadmium Powdered (82), Cadmium Chloride (83), Cadmium Oxide (85), Cadmium Phosphate (86), Cadmium Nitrate (479), Cadmium Potassium Cyanide (480), Cadmium Sulfate (481)

1. GENERAL

Introduction

Cadmium is a metal which is not found as a free mineral in nature. Since pure cadmium is never found in a natural state and cadmium minerals are not found in concentrated form, metallic cadmium is always prepared commerically as a by-product of primary metal industries, principally the zinc industry. Cadmium is found not only in zinc ore but in lead ore, copper ore and other ores that contain zinc minerals. It is intimately associated with the zinc and when ores containing several minerals are separated, the cadmium remains with the zinc. Since the separation process is not exact, lead concentrate will contain a small quantity of zinc and a proportionally small amount of cadmium.

Cadmium compounds contain the element mainly in the divalent state. Cadmium ions in solution react with carbonates, phosphates, arsenates, oxalates, and ferrocyanides to form white precipitates, usually highly hydrated, whose physical characteristics vary with the conditions of precipitation.

In 1968 about 96 percent of the cadmium produced in the United States was primary cadmium and 4 percent was from secondary production - 45 percent recovered from foreign ores; 36 percent from domestic ores; 15 percent from imported flue dust; 4 percent secondary metal derived from reprocessing scrapped alloys.[1086]

Cadmium in zinc concentrates from domestic mines is estimated at 5,304,000 lb/year. This is based on mine production of recoverable zinc, a zinc recovery efficiency of 83 percent and an average of 0.227 percent cadmium contained in 60 percent zinc concentrates. Cadmium in imported zinc ores is estimated at 6,208,000 lb/year.[1086]

In 1969, 12,646,000 lb of cadmium were produced in the United States.[1751] This figure includes cadmium metal and equivalent metal content of cadmium sponge used directly in production of compounds. Cadmium potassium cyanide was produced in very small quantity by City Chemical Company of Jersey City, New Jersey--they are not producing it anymore. They were the only company producing the compound and they only made about 5 or 10 lb of the chemical per year.[2219] Individual production figures for the other cadmium compounds discussed in this profile report are not available.

Manufacture

Cadmium Metal. Cadmium containing ore is mixed with sodium chloride and coal or coke and heated in a sintering furnace. By subjecting the ore to this chloridizing sinter, nearly complete elimination of cadmium as the chloride can be attained and most of it can be recovered. The dust from the roasters and the chloride fume are digested with sulfuric acid. Any lead present is filtered off as the sulfate and metallic cadmium is precipitated by the use of zinc dust. The remaining zinc chloride and sulfate solution is returned to the sintering operation. The cadmium is purified by distillation or electrolysis.[2039]

The purification of zinc sulfate solutions for lithopone or pigment zinc sulfide manufacture produces some cadmium by zinc dust treatment. Manufacturers of electrolytic zinc also produce considerable cadmium during their purification of zinc solutions in a similar way.

Some cadmium is volatilized in lead smelting and is caught in the flue system, particularly in the bag houses. If present in sufficient quantity, the dust is treated for cadmium recovery, usually by solution in sulfuric acid, followed by zinc dust precipitation.[2039]

Large-scale commercial facilities for the manufacture of cadmium metal include the following:[0624]

Amax; Blackwell, Oklahoma
Asarco; Denver, Colorado
Asarco; Corpus Christi, Texas
American Zinc Company; East St. Louis, Illinois
Anaconda; Great Falls, Montana
New Jersey Zinc; Depue, Illinois

Cadmium Chloride. The chloride may be made by dissolving the metal in an aqueous solution of hydrogen chloride and evaporating in a stream of hydrogen chloride gas. It may also be made by dissolving the oxide or carbonate in hydrochloric acid.[1433]

Cadmium chloride is produced by the following companies:[0624]

Allied Chemical Corporation; Harcus Hook, Pennsylvania
J. T. Baker Chemical Company ; Phillipsburg, New Jersey
Chemetron Corporation ; New Brunswick, New Jersey
The Harshaw Chemical Company ; Cleveland, Ohio
Mallinckrodt Chemical Works ; St. Louis, Missouri

Cadmium Nitrate. The nitrate is made by dissolving cadmium metal, cadmium oxide, or cadmium carbonate in nitric acid and evaporating to incipient crystallation. The anhydrous compound is made by dehydrating the tetrahydrate.[1433]

Cadmium nitrate is produced by the following companies:[624]

Allied Chemical Corporation; Buffalo, New York
J. T. Baker Chemical Company; Phillipsburg, New Jersey
Chemetron Corporation; Cleveland, Ohio
The Harshaw Chemical Company; Glouscester City, New Jersey
Mallinckrodt Chemical Works; St. Louis, Missouri
The Shepherd Chemical Company; Cincinnati, Ohio

Cadmium Oxide. Cadmium oxide may be made in one of several ways; the pure metal may be distilled in a graphite retort and the vapor permitted to react with air (since the nitride does not form under these conditions, a pure oxide is obtained). This oxide varies in color and should be calcinated at low red heat to give an oxide of uniform color. Cadmium carbonate and cadmium nitrate may be heated to their temperatures of decomposition to form the oxide.[1433]

Commercial facilities for the manufacture of cadmium oxide include the following:[0624]

Allied Chemical Corporation; Marcus Hook, Pennsylvania
American Smelting and Refining Company; Denver, Colorado
J. T. Baker Chemical Company; Phillipsburg, New Jersey

Cadmium Potassium Cyanide. Cadmium potassium cyanide is made by dissolving potassium cyanide in an aqueous solution of cadmium carbonate. The precipitate is collected and washed as crystals.[2219]

Cadmium Phosphate. Cadmium phosphate is prepared by interaction of cadmium nitrate with potassium dihydrogen phosphate in the present of the proper amount of sodium hydroxide.[2039]

Cadmium Sulfate. When cadmium metal, oxide, carbonate, or sulfide is dissolved in solutions of sulfuric acid and cooled or evaporated, cadmium sulfate (hydrate) crystallizes out. The anhydrous compound may be obtained by the reaction of dimethyl sulfate on finely divided cadmium carbonate, nitrate, halides, or oxide.[1433]

Commercial facilities for the manufacture of cadmium sulfate include the following:[0624]

Allied Chemical Corporation Marcus Hook, Pennsylvania
American Smelting and Refining Company Denver, Colorado
The Glidden Company, Baltimore Maryland

Uses

The chief use of cadmium metal in the United States is in electroplating iron and steel. The industrial and commercial applications for cadmium plating are numerous, including; components for aircraft, automobiles, electrical and electronic apparatus, household applicances, radio and television sets, hardware, and fasteners.[1086]

Cadmium metal is also used in pigments, plastics, alloys, and in making nickel-cadmium batteries. These uses represent more than 90 percent of the cadmium metal consumed in the United States in 1968. Smaller quantities, totaling about 1.1 million lb, were used in fungicides, nuclear energy applications, phosphors for television tubes, photography, lithography, process engraving, glass, X-ray screens, compounds for curing rubber, and various other applications.[1086]

The principal application areas of the other five cadmium compounds have been summarized by Athanassiadis (Table 1).[0624]

Sources and Types of Cadmium Wastes

The metals industry is the major source of emissions of cadmium into the atmosphere. Cadmium dusts and fumes are produced in the extraction, refining, and processing of metallic cadmium. Since cadmium is generally produced as a by-product in the refining of other metals, such as zinc, lead, and copper, plants refining these materials are sources of cadmium emissions as well as of the basic metal. Also, because cadmium is present in small quantities in the ores of these metals, cadmium emissions may occur inadvertently in the refining of the basic metal.

Common sources of cadmium air pollution occur during the use of cadmium. Electroplating, alloying, and use of cadmium in pigments can produce local contaminations of the atmosphere. Also, since cadmium is added to pesticides and fertilizers, the use of these materials can cause local air pollution.[0624,1086]

The sources of cadmium wastes as a contaminant in air or water may include the following: (1) cadmium compound manufacturers; (2) manufacture of cadmium-faced bearings; (3) production of alkaline batteries; (4) casting of copper-cadmium alloys; (5) electroplating; (6) use of cadmium pigments (paints); (7) smelting of scrap metal (containing cadmium); (8) welding of cadmium-plated metal parts; (9) pesticides and fertilizers (containing cadmium).[0624]

Physical and Chemical Properties

The physical and chemical properties of cadmium metal and the six cadmium compounds are included in the attached worksheets.

2. TOXICOLOGY

The inhalation of fumes or dusts of cadmium primarily affects the respiratory tract; the kidneys may also be affected. Even brief exposure to high concentrations may result in pulmonary edema and death. Usually the edema is not massive, with little pleural effusion. In fatal cases, fatty degeneration of the liver and acute inflammatory changes in the kidneys have been noted. Ingestion of cadmium results in a gastrointestinal type of poisoning in its symptoms.

Inhalation of the dust or fumes may cause dryness of the throat, coughing, headache, a sense of constriction in the chest, shortness of breath (dyspnea) and vomiting. More severe exposure results in marked lung changes, with persistent cough, pain in the chest, severe dyspnea and prostration which may terminate fatally. X-ray changes are usually similar to those seen in broncho-pneumonia. The urine is frequently dark. These symptoms are usually delayed for some hours after exposure, and fatal concentrations may be breathed without sufficient discomfort to warn the workman to leave the exposure area.[0624,0766]

Ingestion of cadmium results in sudden nausea, salivation, vomiting, diarrhea and abdominal pain. Symptoms begin almost immediately after ingestion.

A yellow discoloration of the teeth has been reported in workers exposed to cadmium. Cadmium oxide fumes can cause metal fume fever resembling that caused by zinc oxide fumes.[0766]

Two studies made by Frank Princi, M.D., in the early 1950's indicate that cadmium may not be as great an industrial hazard as is generally considered.[2211,2212] Most of the deleterious effects of cadmium which have been reported are the result of relatively brief exposures to high concentrations of the substance. It is probable, therefore, that in chronic exposures there is a rapid elimination of cadmium from the body and that there is no cumulative effect. Doctor Princi observed and ran tests on twenty men who, at times, were exposed to cadmium concentrations as high as 31.30 milligrams per cubic meter of air in their work surroundings.[2212] The tests revealed no serious chronic effects in the workmen from continuous exposure to varying concentrations of cadmium (ranging from .04 to 31.3 mg per cubic meter).

The toxicity of cadmium toward fish was examined by Hiltibran.[2210] His data indicated that cadmium can disrupt energy production by the inhibition of oxygen uptake within the cells, and this disruption can occur at relatively low levels (0.0033 micromoles/ml) and be of such severity as to cause the deaths of fishes, particularly the bluegill.

Most quantitative data on the toxicity of cadmium toward fish are based on specific salts of the metal. Expressed as cadmium, these data indicated that the acute lethal level for fish varies from about 0.01 to about 10 mg/liter depending on the test animal, the types of water, temperature, and time of exposure. Cadmium acts synergistically with other substances to increase toxicity. Concentrations of 0.03 mg/liter in combination with 0.15 mg/liter of zinc causes mortality of very young salmon. In a study of adult American Eastern oysters, the eight week TL_m value for cadmium was 0.2 mg/liter and the fifteen week TL_m value was 0.1 mg/liter.[536]

The relative oral LD_{50} values to the rat are 88 mg/kg for cadmium chloride and 72 mg/kg for cadmium oxide. The estimated LC_{50} value for man is 50 mg/cubic meter of air for cadmium oxide. The American Conference of Governmental Industrial Hygienists (1971) recommended a Threshold Limit Value (TLV) in air of 0.2 mg/cubic meter of air for all the cadmium compounds discussed in this report, except for cadmium oxide. The TLV for cadmium oxide is 0.1 mg/cubic meter of air.[0225] The U.S. Public Health Service established the permissible criteria for soluble cadmium in public water supplies as .01 mg/liter.[1752]

3. OTHER HAZARDS

The fire and explosive hazard of cadmium metal is moderate in the form of dust when exposed to heat or flame or by chemical reaction with oxidizing agents.[0766]

Cadmium nitrate is an oxidizing material. In contact with easily oxidizable substances it may react rapidly enough to cause ignition, violent combustion or explosion.[0766]

Other than the toxic effects, the other cadmium compounds discussed in this report present no further problems.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Care should be exercised in handling cadmium and its compounds because of their high toxicity. Any material which comes in contact with the skin should be removed with plenty of soap and water.

Cadmium nitrate should be stored in an area where it will be separated from combustible, organic or other readily oxidizable materials. Any spilled nitrate should be immediately removed and disposed of. All of the cadmium compounds discussed in this report should be stored away from foodstuffs, feeds, or any other material intended for consumption by humans or animals.

Adequate procedures for the transportation of cadmium compounds have been established by the Department of Transportation.[0278] Label requirements as well as the maximum quantities permitted to be shipped in one outside container, are also specified.

Disposal/Reuse

The greater portion of cadmium and cadmium compounds present in air and water waste streams can be removed and the cadmium recovered for its value. With the current technology available, and considering the economic factors involved, it is not possible to remove all of the cadmium that is discharged into waste streams. For these reasons, the safe disposal of cadmium and cadmium compounds must still be defined in terms of the recommended maximum concentrations released to the atmosphere and a potable water source and/or marine habitat(Table 2).

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Removal from Air

The metals industry is the major source of cadmium emissions to the atmosphere. Cadmium dusts and fumes are produced in the extraction, refining, and processing of metallic cadmium. More than 2 millions lb of cadmium were released to the atmosphere by the metals industry in 1968.[1086] Air pollution control procedures are employed at some metal refinery plants in order to recover the valuable cadmium that would otherwise escape into the atmosphere. Electrostatic precipitators, bag houses, and cyclones are effectively used for abatement.[0624] However, little information has been found on the specific application of these procedures for the purpose of controlling cadmium air pollution. Procedures for recovering cadmium from exhaust in a copper extraction plant collected significant quantities of valuable cadmium, at the same time reducing local air pollution levels.[0624]

Removal from Water

Option No. 1 - Adsorption with Granular Activated-Carbon Bed. The effectiveness of granular activated beds to remove cadmium from water has been investigated by Linstedt et al[2218] and Kuzin et al.[1813] Linstedt found in his study that following passage through a column, filled to a depth of 60 in. with 14-40 mesh granular activated carbon, the initial concentration of 50.5 ppb of cadmium was reduced to .6 ppb. This represents a 98.8 percent removal of cadmium from the water. Kuzin's laboratory investigation was principally directed towards the separation of uranium from other metallic compounds in acetate solutions. It was found in the same study, however, that activated carbon possessed a sorption capacity for soluble compounds of 1.9 mg/g carbon. Adsorption with granular activated-carbon beds should be considered as one of the most satisfactory methods for treating dilute cadmium wastes.

Option No. 2 - Coagulation and Filtration. A pilot plant study by Lindstedt et al [2218] showed that coagulation, sedimentation, and filtration could be used to remove about 95 percent of the cadmium in a water supply from a secondary water treatment plant. The concentration of the cadmium in the water before the coagulation process was 5.5 ppb. Coagulation was achieved by slaking commercial-grade lime and pumping it into the influent wastewater flow line. The pH was approximately 11 in the coagulation unit. After lime addition, the wastewater entered a rapid-mix line. The lime feed point was at the head of the line, and mixing was achieved through turbulence of the flow. Slow mixing and settling of the cadmium hydroxide preciptate were achieved in a fiber glass tank equipped with four vertical baffles and a mixing blade. It can be concluded that chemical coagulation followed by sand filtration is an adequate method for removing cadmium from water.

Option No. 3 - Ion Exchange. Ion exchange can be used to remove cadmium from dilute aqueous waste streams. Cadmium will behave much like calcium and magnesium and can be removed from an aqueous waste stream by either a sulfonic acid type cation excnange resin or a carboxylic weak acid type resin, depending upon the pH of the stream.[1795] The effectiveness of ion exchange to remove cadmium from water has been investigated by Linstedt et al.[2218] Linstedt found that the initial concentration of 50.5 ppb of cadmium in the water was reduced to .76 ppb. This represents a 98.5 percent removal of cadmium from the water. The major difficulty in ion exchange operation is the critical dependence on flowrate. The ion exchange system is designed to operated with a particular efficiency at a certain set flow. Should this flow be exceeded, the efficiency for adsorbing the cadmium ion decreases drastically causing the effluent to exceed the permissible limit.

Option No. 4 - Reverse Osmosis. The effectiveness of reverse osmosis to remove cadmium from water has been investigated by Sourirajan.[1812] Following passage of a cadmium waste stream through a porous cellulose acetate membrane, it was found that the cadmium concentration was reduced from 59.1 ppm to 11.2 ppm. This represents an 81 percent removal of cadmium from the water. With an effluent concentration of 11.2 ppm, the reverse osmosis unit would have to be used in conjunction with some other process (adsorption with activated carbon for example) to produce an effluent with a permissible concentration of cadmium.

The other treatment processes for the removal of cadmium from water that have been investigated include adsorption with zirconium phosphate, silica gel and charcoal. Akatsu et al [2220] demonstrated that the cadmium ion was only slightly adsorbed by zirconium phosphate and charcoal and not adsorbed at all by silica gel. These processes are therefore considered as inadequate methods for treating dilute cadmium wastes.

Concentrated Cadmium Wastes

The only adequate method for the disposal of concentrated cadmium wastes is coagulation with lime, then sedimentation followed by sand filtration. The effluent from this process would probably have to be treated further (adsorption with activated carbon or ion exchange for example) to reduce the cadmium concentration to a level in compliance with the U.S. Public Health Service recommendation for public drinking water (.01 mg/liter). The cadmium hydroxide sludge produced in this process can be dried and placed in an approved chemical landfill area. Cadmium hydroxide is not very soluble (.0026g/100cc), so contamination of water supplies from the landfill operation should not be a problem. If the cadmium hydroxide sludge is relatively pure, it can be dissolved in sulfuric acid and the cadmium metal recovered by zinc dust precipitation (refer to section on Manufacture).

6. APPLICABILITY TO NATIONAL DISPOSAL SITE

It is anticipated that disposal systems to handle both dilute and concentrated cadmium wastes will be required at National Disposal Sites. The processes recommended for the treatment of dilute cadmium wastes at National Disposal Sites are:

Process	Order of Preference	Remarks
Activated-Carbon Beds	First Choice	Demonstrated technology; recommended unit operation at National Disposal Sites.
Coagulation and Filtration	Second Choice	Demonstrated technology; can be effectively used to remove both dilute and concentrated cadmium wastes.
Ion Exchange	Third Choice	Demonstrated technology; critical dependence on flowrate and economic factors limit the feasibility of this system.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

81
82

H. M. Name Cadmium

IUC Name

Common Names Cadmium

Structural Formula

Cd

Molecular Wt. 112.41 Melting Pt. 320.9 C Boiling Pt. 767

Density (Condensed) ____ @ ____ ____ Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55°C and 20°C)

1 MM @ 394 C ____ @ ____ ____ @ ____

Flash Point ____ Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water insolulbe Hot Water insoluble Ethanol ____

Others: hot sufluric acid, ammonium nitrate

Acid, Base Properties ____

Highly Reactive with ____

Compatible with ____

Shipped in ____

ICC Classification ____ Coast Guard Classification ____

Comments ____

References (1) 0766

83

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Cadmium Chloride

IUC Name

Common Names

Structural Formula

$CdCl_2$

Molecular Wt. 183.32 Melting Pt. 568 C Boiling Pt. 960 C

Density (Condensed) 4.047 @ 25 C Density (gas) @

Vapor Pressure (recommended 55°C and 20°C)

10 MM @ 656 C 100 MM @ 797 C @

Flash Point N/A Autoignition Temp. N/A

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 90 g/100 g @ 0 C Hot Water 147 g/mg @ 100 C Ethanol slightly soluble

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments Hexagonal, colorless crystals

References (1) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

85

H. M. Name Cadmium Oxide

IUC Name ______

Common Names Cadmium Oxide
(1) amorphous, brown crystals
(2) cubic, brown crystals

Structural Formula

CdO

Molecular Wt. 128.41 Melting Pt. (1)1,495C; (2)900C Boiling Pt. 1559C

Density (Condensed) 6.95 / 8.15 @ ____ ° ____ Density (gas) ______ @ ______ ______

Vapor Pressure (recommended 55 C and 20 C)

1MM @ 1000C ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water Insoluble Hot Water Insoluble Ethanol ______

Others: Ammonia salts

Acid, Base Properties ______

Highly Reactive with ______

Compatible with ______

Shipped in ______

ICC Classification ______ Coast Guard Classification ______

Comments ______

References (1) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

86

H. M. Name Cadmium phosphate

IUC Name Cadmium ortho-phosphate

Common Names

Structural Formula

$Cd_3(PO_4)_2$

Molecular Wt. 527.19 Melting Pt. 1500 C Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble Hot Water Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1)0766

#479

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Cadmium Nitrate

IUC Name

Common Names

Structural Formula

$Cd(NO_3)_2$

Molecular Wt. 236.43 Melting Pt. 350 C Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 109g/100cc Hot Water 326g/100 cc Ethanol Soluble

Others: Acids; ethyl acetate

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 1492

480

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Cadmium Potassium Cyanide

IUC Name

Common Names Cadmium Potassium Cyanide

Structural Formula

$Cd(CN)_2 \cdot 2KCN$

Molecular Wt.[1] 294.68 Melting Pt.[2] Boiling Pt.

Density (Condensed) 1.847 @ Density (gas) @

Vapor Pressure (recommended 55°C and 20°C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 33.3 g/100CC Hot Water 100g/100 CC Ethanol Insoluble

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments When heated, melts to a colorless liquid solidifying to a grey, crystaline mass on cooling.

References (1) 1492

where necessary

HAZARDOUS WASTES PROPERTIES
WORKSHEET

481

H. M. Name Cadmium Sulfate

IUC Name

Common Names Cadmium Sulfate

Structural Formula

$CdSO_4$

Molecular Wt. 208.46 Melting Pt. 1000C Boiling Pt.

Density (Condensed) 4.691 @ 20C 4C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 75.5g/100CC Hot Water 60.8g/100CC Ethanol insoluble

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 1492

TABLE 1[0624]

APPLICATION AREAS OF CADMIUM COMPOUNDS

Compound	Uses
Cadmium Chloride	In photography; in dyeing and calico printing; in the vacuum tube industry; in manufacture of cadmium yellow; special mirrors; as ice nucleating agent; lubricant; in analysis of sulfides to absorb the hydrogen sulfide.
Cadmium Nitrate	In making other cadmium salts; in photographic emulsions.
Cadmium Oxide	In phosphorus, semiconductors, manufacture of silver alloys, glass; in storage battery electrodes; as nematocide; as catalyst for organic reactions; in cadmium electroplating; in ceramic glazes.
Cadmium Phosphate	Similar uses to those of normal phosphate.
Cadmium Sulfate	In electrodeposition of Cd, Cu, and Ni; in phosphors; in manufacture of standard cadmium elements.

TABLE 2. RECOMMENDED MAXIMUM CONCENTRATIONS

Contaminant In Air	Maximum Recommended Concentration	Basis for Recommendation
Cadmium Metal (powder)	.002 mg/cubic meter/24 hours	.01 TLV
Cadmium Chloride	.002 mg/cubic meter/24 hours	"
Cadmium Nitrate	.002 mg/cubic meter/24 hours	"
Cadmium Oxide	.001 mg/cubic meter/24 hours	"
Cadmium Potassium Cyanide	.002 mg/cubic meter/24 hours	"
Cadmium Phosphate	.002 mg/cubic meter/24 hours	"
Cadmium Sulfate	.002 mg/cubic meter/23 hours	"

Contaminant In Water	Maximum Allowable Concentration in Point Sources	Basis for Recommendation
Cadmium Metal (powder)	.01 mg/liter	U.S. Public Health Service recommendation for public drinking water
Cadmium Chloride	.01 mg/liter	"
Cadmium Nitrate	.01 mg/liter	"
Cadmium Oxide	.01 mg/liter	"
Cadmium Potassium Cyanide	.01 mg/liter	"
Cadmium Phosphate	.01 mg/liter	"
Cadmium Sulfate	.01 mg/liter	"

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PROFILE REPORT

Chloroacetophenone (107) Tear Gas (CN) (422)

1. GENERAL

Chloroacetophenone, also known as tear gas (CN), is a very effective solid lachrymator produced by chlorination of acetophenone or by a Friedel-Crafts reaction of benzene with chloroacetyl chloride. The chlorination of acetophenone is accomplished by direct reaction with chlorine in acetic acid solution or with selenium oxychloride in a benzene solution. In the Friedel-Crafts reaction, chloroacetyl chloride is added to benzene in the presence of aluminum chloride catalyst.[0778,1492,1662]

Chloroacetophenone is relatively stable and slow to react. It will react with most of the usual compounds that couple with the aliphatic carbonyl group such as hydroxylamine and hydrazine. However, sodium bisulfite does not react with chloroacetophenone. It is stable when exposed to detonation and has good thermal stability up to 300 C.[0788] The physical/chemical properties for chloroacetophenone are summarized in the attached work sheet.

2. TOXICOLOGY

In very low concentrations in air chloroacetophenone has an odor resembling apple blossoms. An intolerable level is considered to be 4.5 mg per cubic meter while a concentration of 850 mg per cubic meter is estimated to be lethal. The symptoms include tearing, burning of the eyes, and difficulty in breathing. The TLV (ACGIH) is 0.3 mg per cubic meter (0.05 ppm)[0766].

3. OTHER HAZARDS

When chloroacetophemone is heated to decomposition, it emits toxic fumes. It reacts slowly with steam to produce toxic and corrosive fumes.[0766]

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4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Though the vapor pressure of chloroacetophenone is relatively low (equilibrium concentration at 20 C is 0.11 mg/l), the vapor pressure which develops is sufficient to make a terrain contaminated with it impassible without a protective mask. The fact that chloroacetophenone does not decompose at its own boiling point makes it possible to pour the melted compound directly into shells and to mix the material with explosives such as TNT. It is a persistent lachrymator. Solutions of tear gas (CN) spread on the terrain may retain their effects for hours or days.[0778]

When working with chloroacetophenone ventilation control must be maintained. Self-contained breathing masks must be available and protective clothing and rubber gloves worn.[1141] Chloroacetophenone is shipped in glass bottles under DOT regulations for Class C poison requiring a tear gas label.[0766] Recommended maximum concentrations of chloroacetophenone in effluent streams released to the environment from waste disposal processes are as follows:

Contaminant and Environment	Maximum Allowable Concentration	Basis for Recommendations
Chloroacetophenone released to atmosphere	0.0005 ppm (0.003 mg/M^3)/24-hr	0.01 TLV
Chloroacetophenone placed on soil	zero	Persistent up to weeks at low temperatures
Chloroacetophenone released to aqueous streams	zero	At ordinary temperatures hydrolysis does not take place, and CN persists indefinitely.

5. EVALUATION OF CURRENT AND NEAR FUTURE CHLOROACETOPHENONE DISPOSAL PROCESSES

Chloroacetophenone is expected to appear primarily as a packaged waste, in a mixture such as MACE, or with explosives whose composition is known.

The processing options are briefly described in the following paragraphs together with recommendations as to their adequacy.

Option No. 1 - Incineration.

When chloroacetophenone and mixtures of chloroacetophenone are packaged with easily combustible materials, the process recommended by the Manufacturing Chemist's Association appears to be satisfactory.[1141] The chloroacetophenone-containing-waste is dissolved in an organic solvent (usually benzene or an alcohol) and sprayed into an incinerator equipped with an afterburner and alkali scrubber.

Option No. 2 - Reaction with Sodium Sulfide.

Chloroacetophenone reacts with sodium sulfide in alcoholic or alcohol-water solutions to form bis-(acetylphenyl)-thioether (melting point 74 C) which shows no physiological effect.[0778] This process is attractive because it not only converts the chloroacetophenone into a compound that has no physiological effect, but explosive nitro compounds, when present, are decomposed to nonexplosive compounds. This process results in the liberation of hydrogen sulfide, which must be collected by an alkaline scrubber. The alcohol solution containing the decomposed compounds may be sprayed into an incinerator equipped with an alkali scrubber to remove any hydrogen chloride, NO_x, and sulfur oxides formed.

Option No. 3 - Reaction with Sodium Thiosulfate.

By boiling in an alcohol-water solution with sodium thiosulfate the sodium salt of acetylphenyl thiosulfonic acid is obtained.[0778]

$$C_6H_5COCH_2 \cdot S_2O_3Na$$

The thiosulfonate solution must then be sprayed into an incinerator equipped with an alkali scrubber. This process converts the chloroacetophenone into a compound that shows no physiological effect, but incineration of the thiosulfonate is required which does not in most cases offer any advantages over Options No. 1 and No. 2.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Chlorcacetophenone in small quantities as a packaged waste and as a mixture with other materials is expected to require disposal. It is anticipated that the expertise required for treating a lachrymator will not be available at the source of the waste generation. Therefore, chloroacetophenone is judged to be a candidate for National Disposal Sites. Disposal processes recommended are those of Option No. 1 or Option No. 2.

7. REFERENCES

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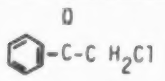
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chloroacetophenone

IUC Name W-Chloroacetophenone

Common Names Phenacyl Chloride

Structural Formula



$C_6H_5-\overset{O}{C}-CH_2Cl$

Molecular Wt. 154.6(1)   Melting Pt. 58-59C(2)   Boiling Pt. 139-141 C(2)

Density (Condensed) 1.321 @ 20C   Density (gas) ____ @ ____

Vapor Pressure (recommended 55 C and 20 C)

0.012 torr @ 0   0.16 Torr @ 50 C   ____ @ ____

Flash Point ____   Autoignition Temp. ____

Flammability Limits in Air (wt %)   Lower ____   Upper ____

Explosive Limits in Air (wt. %)   Lower ____   Upper ____

Solubility

Cold Water 0.1% (w/w)(2)   Hot Water ____   Ethanol Soluble (2)

Others: Soluble, ether, benzene(2)

Acid, Base Properties None

Highly Reactive with Hydroxyamine (2)

Compatible with most materials of construction

Shipped in Bottles(1)

ICC Classification Class C Poison(1)   Coast Guard Classification Class C Poison(1)

Comments ____

References (1) 1301
(2) 0778

PROFILE REPORT

Chlorosulfonic Acid (112)

1. GENERAL

Chlorosulfonic acid is an important item of commerce, tank-car quantities being used as an intermediate in the production of synthetic detergents, drugs, ion exchange resins, and dyestuffs. It has also been used as a smoke-forming agent in warfare. Chlorosulfonic acid may be considered as a mono acid chloride of sulfonic acid, since one chlorine atom has replaced one hydroxyl group. It is a clear, colorless, mobile liquid which decomposes slightly when distilled. It reacts with water with explosive violence and fumes strongly in moist air to form a persistent, irritating aerosol of sulfuric and hydrochloric acids. It also reacts with almost all organic materials; in some cases with charring.

Chlorosulfonic acid is a strong acid containing a relatively weak sulfurchlorine bond. It is a powerful sulfating and sulfonating agent, a fairly strong dehydrating agent, and a specialized chlorinating agent. In most of its applications it is used to form sulfates, sulfonates and sulfonyl chlorides with such organic compounds as hydrocarbons, alcohols, phenols and amines. Many salts and esters of chlorsulfonic acid are known, but most of them are relatively unstable or hydrolyze readily in moist air.

Manufacture of chlorosulfonic acid is accomplished by the direct union of sulfur trioxide with dry hydrogen chloride gas. The sulfur trioxide may be in the form of 100 percent liquid or gas, as obtained from boiling oleum, or may be present as a dilute gaseous mixture obtained directly from a contact sulfuric acid plant. The reaction of sulfur trioxide and hydrogen chloride takes place spontaneously with evolution of a large quantity of heat.[1433] The chemical/physical properties for chlorosulfonic acid are given in the attached work sheet.

2. TOXICOLOGY

Chlorosulfonic acid will cause severe acid burns on contact of the liquid with the skin or mucose, and the vapor is very irritating to the eyes, lungs, and mucous membranes. It can cause acute toxic effects in either the liquid or vapor state. Inhalation of concentrated vapor may cause loss of consciousness with serious damage to lung tissue. Upon ingestion, it will burn and destroy the mucose of the mouth, esophagus and stomach to a serious degree. Contact of the liquid with the eyes can cause permanent destruction of the tissues involved. Even in the vapor state it causes conjunctivitis.[0766] Chlorosulfonic acid does not have a Threshold Limit Valve (TLV) established by the American Conference of Governmental Industrial Hygienist (ACGIH) but the TLV of 5 ppm for hydrochloric acid should be considered the maximum levels of exposure for an 8-hr work day of a 40-hr work week.[0095]

3. OTHER HAZARDS

Chlorosulfonic acid is corrosive, functioning both as a strong acid and as a dehydrating and charring agent. It has an appreciable vapor pressure and through the action of moisture in air (or water) is decomposed to hydrochloric acid and sulfuric acid. Good ventilation should be provided, and goggles, gloves, protective clothing, and face shields should always be worn when handling this material.

The acid itself is not flammable, but may cause ignition by contact with combustible materials. The flammable and explosive gas, hydrogen, is slowly generated by action of the acid on moist metals.[1433]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

When working with chlorosulfonic acid waste or spills, in addition to the protective devices indicated above, a self-contained breathing apparatus should be employed. For small quantities work can be performed in a fume hood, and a laboratory coat, goggles and gloves should be worn. Spills of small quantities should be covered with excess sodium bicarbonate and the mixture diluted with a large quantity of water. Spills of larger quantities should very carefully be diluted with a large quantity of water and neutralized with lime.[0095]

Chlorosulfonic acid is shipped in bottles, 170-lb carboys, 1,600-lb stainless steel drums and 8,000-gal tank cars. It is shipped under DOT regulations as a corrosive liquid requiring a White Label.[1416]

Recommended maximum concentrations for chlorosulfonic acid and the usual reaction products formed during disposal processes in effluent streams released to the environment are as follows:

Contaminant and Environment	Maximum Concentration at Point Source	Basis for Recommendation
Chlorosulfonic acid released to the air inside the boundaries of the processing plant.	5 ppm	TLV for HCl which is formed upon contact with moisture. 0095
Chlorosulfonic acid released to the air outside the boundaries of the processing plant.	0.05 ppm	0.01 of TLV for HCl
ph of water after contact with chlorosulfonic acid, followed by neutralization with lime.	6.5 to 9.0	Allowed limits of effluent being discharged to a storm sewer or stream. 0536
Chloride ion content of water after contact with chlorosulfonic acid.	150 ppm	Maximum allowed concentration in an effluent being discharged to a storm sewer or stream. 0536
Sulfate ion content of water after contact with chlorosulfonic acid.	250 ppm	Maximum allowed concentration in an effluent being discharged to a storm sewer or stream. 0536

5. EVALUATION OF CURRENT AND NEAR FUTURE CHLOROSULFONIC ACID DISPOSAL PROCESSES

The method of disposal of packaged lots of chlorosulfonic acid recommended by the Manufacturing Chemists Association is satisfactory if the effluent from the disposal process is within the limits for pH, chloride ion, and sulfate ion listed in Section 4.

In this procedure chlorosulfonic acid is decomposed by pouring small quantities from behind a shield onto a dry layer of sodium bicarbonate. After mixing the sodium bicarbonate thoroughly, the sodium bicarbonate while being stirred is sprayed with 6M ammonium hydroxide. Then the sodium bicarbonate is covered with a layer of crushed ice; and while continued to be stirred, the sodium bicarbonate is again sprayed with 6M ammonium hydroxide. When evolution of ammonium chloride, which must be vented, has partially subsided, the sodium bicarbonate solution is neutralized with hydrochloric acid. Then after dilution to the concentration permitted for effluents (see Section 4), the treated solution is discharged into a stream or storm sewer.[0095]

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is anticipated that the great majority of chlorosulfonic waste will continue to be best handled at the source of the waste generated. Because the process requires little special equipment and when performed properly, no new very toxic materials are created, chlorosulfonic acid does not appear to be a candidate for a National Disposal Site.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chlorosulfonic Acid

IUC Name Chlorosulfonic Acid

Common Names Sulfuric Chlorohydrin

Structural Formula

$ClSO_3H$

Molecular Wt. 11.653 Melting Pt. -80C Boiling Pt. 151.0C

Density (Condensed) 1.766 @ 18 C Density (gas) - @ °

Vapor Pressure (recommended 55 C and 20 C)

1 torr at 32 C @ ° @ °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water reacts Hot Water reacts violently Ethanol reacts

Others:

Acid, Base Properties Upon contact with water forms hydrochloric or sulfuric acid.

Highly Reactive with Most organic materials; water

Compatible with

Shipped in Carboys, 1600 pound drums, 8,000 gallon tank cars

ICC Classification corrosive liquid Coast Guard Classification corrosive liquid

Comments Extremely caustic, corrosive and toxic liquid.

References (1) 1416

PROFILE REPORT

Lead (233)

1. GENERAL

Lead is a soft, heavy, bluish-gray metal. Its surface oxidizes readily, and is then very resistant to corrosion. It is soluble in nitric acid and in many organic acids, but not in dilute sulfuric or hydrochloric acid, and is one of the most stable metals. Lead and its compounds are cumulative poisons and should not be used in contact with foods. It is used for containers and tank linings for many corrosive liquids, such as sulfuric acid. Lead as the metal and as the dioxide is used in large quantities in storage batteries. The metal and its alloys are used in solders, type metal, bearings, pipe, cable covering, plumbing, ammunition, and in the manufacture of tetraethyl- and tetramethyl lead. It is also used as a sound absorber and as a radiation shield.

Lead ores are usually sulfides (galena, PbS), oxides, or carbonates. By means of complicated flotation, leaching, and smelting processes, lead is recovered from its ores. Lead not recovered will generally end up in slag piles.[1433]

The chemical/physical properties of lead are summarized in the attached worksheet.

2. TOXICOLOGY

Lead is present in the individual's normal environment. The daily intake of lead in the food and beverage of American adults is about 0.3 mg. The human body is capable of eliminating this amount daily. However, if more lead is taken into the system than is eliminated, a condition exists which is referred to as "chronic lead poisoning."

Initially, the symptons of lead intoxication usually take the form of weakness, pains in the joints, severe constipation, and colic-like pains. Exposure over longer periods of time will frequently intensify the pains in the joints and the weakness of the muscles. Acute attacks of colic will develop.[0766]

Lead may enter the human system through inhalation, ingestion, or skin contact. Industrially, inhalation of dust, mist, or fumes is the chief method by which lead and its inorganic compounds may enter the body. In practice, the amount of lead or its inorganic compounds in the work atmosphere should not exceed an average of 0.2 mg of lead per cubic meter for an 8-hr working day of a 40-hr work week (TLV). Ingestion is not an important form of lead exposure in the present-day industrial establishment when care is taken to avoid its contact with food.[1699] Direct skin contact is of negligible importance in connection with inorganic lead compounds. However, in the case of organic lead compounds, skin contact can be a real hazard.[0766]

The toxicity of lead and its inorganic compounds varies with several factors of a chemical and physical nature. The most important considerations are the form in which the lead is present, the particle size, and the length of exposure time. The fineness of the lead-containing particles is of great importance. Particles above 10μ are frequently not absorbed in the lungs at all and are screened out by the nasal mucosa and hairs. It is generally only particles below 5μ that are retained to any extent, and retention is at a maximum below 1μ. Plants handling lead must, therefore, take care to avoid creating fine lead particles; or if produced, personnel must be protected from fine dusts.[0766]

3. OTHER HAZARDS

Lead does not usually present any special hazards other than those associated with its Toxicology.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Lead is insoluble in water and therefore, its use in pipes and as a joint dope is harmless with most water supplies. Some waters do dissolve lead from plumbing, but the reasons are not known. Naturally soft waters which are slightly acid and low in mineral content are the most corrosive and should not be used with lead plumbing. When lead compounds are used in ceramic glazes, lead is solubilized and extracted by the organic acids present in food and the use of lead compounds in glazes is therefore a serious hazard. A maximum level with respect to extractable lead in ceramic glazes is 7 mg per milliliter, released after extracting a piece of dinnerware for 24 hours at room temperature in a 4 percent acetic acid solution.[1699] Atmospheric lead contamination by discharge from (1) primary and secondary lead smelters, (2) combustion of coal and fuel, (3) incineration, and (4) combustion of gasoline containing lead antiknock additives is a serious health problem.[1699]

Lead is usually shipped as pigs or in fabricated form. There are no special regulations governing the transportation of lead.

Recommended maximum concentration of lead in effluent streams released to the environment are as follows:

Effluent and Environment	Maximum Concentration at Point Source	Basis for Recommendation
Lead released to the air as particulate material inside the boundaries of the processing plant	0.2 mg per cubic meter	TLV[1699]
Lead released to the air as particulate outside the boundaries of the processing plant	0.002 mg per cubic meter	0.01 TLV
Lead released, in any form, in water to natural streams or sewers	0.1 mg per liter	Level above which bacterial decomposition of organic matter is inhibited.[1966]

5. EVALUATION OF CURRENT AND NEAR FUTURE LEAD DISPOSAL PROCESSES

Recent estimates indicate that 42 percent of all lead is reclaimed with the remainder remaining in use or lost in dumps or to the environment in an uncontrolled manner. The chief sources of reclaimed scrap include automobile storage batteries, cable sheathing, plumbing pipes, sheets, solder, joint caulking, type metal, freight car bearings, loaded brass and bronzes, spent ammunition, discarded ballast, foil, and blast furnace matte. Reclamation and processing of scrap are less costly sources of lead metal than mining and smelting primary lead, and replaces primary lead production to the extent available. Processes for reclaiming lead from scrap or blast furnace matte are briefly discussed in the following paragraphs together with recommendations as to adequacy.

Current Processes

Option No. 1 - Melting into Ignots. If scrap lead is pure, it is melted and cast into ignots for sale and shipment.[1699] The off gas from furnaces used to melt lead is cooled by air dilution and then filtered by a cloth bag dust collector used in conjunction with other dust collecting equipment such as a cyclone.[0635, 0673] The particulate matter is then returned to the furnace. When the scrap is pure or nearly pure lead, this is obviously the recovery method of choice.

Option No. 2 - Recovery in Lead Blast Furnace. Blast furnaces used for smelting lead ore are also used for the secondary recovery of lead from such sources as battery plates. In a blast furnace, scrap lead to be recovered along with a mixture of roasted and part unroasted ore is charged to the furnace with iron oxide, silica and carbon. Upon heating, the copper present collects in the iron sulfide matte (which also contains 0 to 18 percent lead) while other metals remain in the lead. In refinement of the crude blast furnace lead, the more electropositive impurities are removed by air oxidation from frequent stirring of the molten lead over a several hour period. The impurities, when oxidized, rise to the surface and are skimmed off. Off gas from smelting plants is cooled by air dilution and then filtered by a cloth bag dust collector used in conjunction with other dust collecting equipment such as a cyclone.[0635,0673] The particulate matter is then returned to the smelter. If the lead contains appreciable quantities of bismuth, the lead is purified electrolytically.[1326] These custom smelting plants provide the most efficient and economical means for the recovery of lead. For efficient operation, a smelting plant requires a continuous supply of raw materials which can best be supplied with a mixture of primary and secondary lead. Also, a smelting plant requires a large capital expenditure which can only be justified by a large continuous operation. The use of smelters is recommended because more than 80 percent of the secondary lead is recovered by this means.[1326]

Option No. 3 - Recovery from Blast Furnace Matte. A process developed by the Bureau of Mines at the College Park Metallurgic Research Center recovers lead and copper from lead matte.[0128] In this process, all the sulfides are first oxidized to sulfates by roasting, so that subsequent water leaching of the roasted products will extract the copper and other water-soluble salts. The copper is recovered from solution by cementing with iron powder. The water-insoluble residue is treated with a saturated brine solution to dissolve lead as a lead chloride complex while the associated sulfate ion is rendered insoluble by formation of calcium sulfate upon treatment with lime. The dissolved lead is then precipitated as $3\ PbO \cdot PbCl_2$ by the addition of more lime. An alternate method that does not require roasting involves oxidation by the bacterium Ferrobacillus ferrooxidans in dilute sulfuric acid solution or by air oxidation of a dilute sulfuric acid leach. The lead and copper sulfates are recovered as described above. The lead oxide is reduced by treatment at high temperature with carbon or carbon monoxide.

Option No. 4 - Assignment to Land Fills. Because lead is insoluble in water and not attacked by most inorganic acids or bases, lead in small quantities is often disposed of in landfills.[0095] Though this disposal method is satisfactory under most conditions, it is not recommended because lead is lost to future use. In addition, under certain conditions, lead is solubilized as either the chloride or the sulfate, which are both slightly soluble in water.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Lead present in most waste forms or lead alloys can best be recovered by returning the lead-containing wastes to blast furnaces designed for processing primary lead. Numerous companies purchase or salvage scrap lead which is then sold to primary lead processors.[1326] Therefore, processes for the recovery of lead are not a candidate for National Disposal Sites.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Lead

IUC Name Lead

Common Names Plumbum

Structural Formula

Pb

Molecular Wt. 207.21 Melting Pt. 327.43 C Boiling Pt. 1740 C

Density (Condensed) 11.3437g/cc @ 20 C Density (gas) - @ °

Vapor Pressure (recommended 55 C and 20 C)

1.0 torr @ 987 C 10 torr @ 1167 C 100 torr @ 1417 C

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble Hot Water insoluble Ethanol insoluble

Others: soluble-nitric acid, most organic acids

Acid, Base Properties

Highly Reactive with most organic acids in presence of oxygen.

Compatible with most inorganic acids and bases except nitric acid.

Shipped in pigs

ICC Classification none Coast Guard Classification none

Comments

References (1) 1433

PROFILE REPORT ON
MERCURY AND INORGANIC MERCURY COMPOUNDS
Mercury (257), Mercuric Chloride (253),
Mercuric Nitrate (255), Mercuric Sulfate (256),
Mercuric Diammonium Chloride (503)

1. GENERAL

Introduction

Mercury, commonly called quicksilver, was one of the first metals known to man and has been mined at Almaden, Spain for 27 centuries. In earlier times, mercury has been mainly used as a decorative (in the form of cinnabar), as a medical ointment for skin diseases, and as an amalgam for tin and copper. Introduction of mercury into scientific research occurred in 1643, with the invention of the barometer by Torricelli. This was followed in later years by the invention of the mercury thermometer, the discovery of the use of mercury as a seal for water-soluble gases in gas analysis, and the preparation of mercury fulminate as a detonator for explosives. Because of the relatively small scale use of mercury in the past, mercury and mercury compounds were never considered a real threat to the quality of the environment, although the toxic nature of mercury and its compounds have been known for centuries. Mercury today, however, is used on a substantial scale in chemical industries, in the manufacture of paints and paper, in pesticides for agriculture, and in the electrical industry. With the development of these applications, and the failure to recognize the hazards associated with seemingly harmless levels of mercury and inorganic mercury compounds, came serious problems.

First in 1960, it was reported that 111 persons had died or suffered serious neurological damage near Minamata, Japan, as a result of eating fish and shellfish which had been contaminated by methyl mercury and mercuric chloride discharged into Minamata Bay by a plastics manufacturing plant. In 1965, another poisoning incident was reported in Niigata, Japan, and in 1966, Swedish studies showed that many species of birds were being poisoned by mercury. Finally, in the spring of 1970, high levels of mercury were discovered in fish in Lake St. Clair, on the Canada-United States border. Canada banned the sale of fish from the lake, and 10 days later Michigan followed suit. In succeeding months, there followed a series of bans on fish and seafood containing excessive mercury, legislations against discharge of mercury into navigable waters, and the cancellations of Federal registrations of numerous mercury compounds for industrial and agricultural uses.

It was these several spectacular reported incidents of mercury poisoning in recent years, and the positive demonstration that inorganic mercury could be biologically methylated in the natural aquatic environment and subsequently concentrated up to 3,000 times in fish and other marine organisms, that finally led to the full realization of the extent of the mercury pollution problem.

The quantity of mercury used each year in the world increased at a rate of about 1,800 flasks* per year for the ten-year period previous to 1968. Most of the increase was due to the U.S. demand, which grew at a rate of 1,600 flasks per year over the same period until in 1968 it represented about 30 percent of the world primary production of 257,000 flasks. Also in 1968, the U.S. supply of mercury came from four sources: 18 percent from recycled material; 36 percent from U.S. mining; 22 percent from net imports; and 24 percent from Government stockpile releases.[2105] Individual statistics for the production and consumption of inorganic mercury compounds are not available, but could be estimated from the consumption figures of mercury by uses (Table 1).

Manufacture

Mercury. The most common metallurgical process for recovering mercury is that of roasting cinnabar (mercuric sulfide) in either mechanical furnaces or retorts to volatilize the mercury followed by condensation of the vapor. Furnacing is a continuous operation where the mercury bearing materials are directly heated by the gases of combustion, and has the disadvantage of involving large volumes of furnace gas. Retorting, on the other hand, is a batch operation where the material is heated indirectly and consequently the volume of retort gas is small.[1433] Hydrometallurgical processes for extracting mercury include leaching with either sodium hypochlorite or sodium sulfide, but to date both methods have not been commercially employed for the recovery of mercury.[2064] The major U.S. producers of mercury include the following:[0637]

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*A flask contains 76 lb mercury and is the standard commercial unit of trade.

Decoursey Mountain Mining Company; Anchorage, Alaska
Harold Braggini; Atascadero, California
COG Minerals Corp.; Denver, Colorado
New Idria Mining and Chemical Co.; Guerneville, California
Holly Minerals Corp.; Albuquerque, New Mexico
Rare Metals Corp. of America; Salt Lake City, Utah
Cordero Mining Co.; Palo Alto, California
Arentz-Comstock Mining Venture; Salt Lake City, Utah
Bonanza Oil and Mining Corp.; Sutherlin, Oregon

Mercuric Chloride. Mercuric chloride is produced commercially by the direct chlorination of mercury. Older processes, based on the reaction between mercurous sulfate and sodium chloride, are no longer extensively practiced in the United States.[1433]

Mercuric Nitrate. Mercuric nitrate is made by dissolving mercury in an excess of hot concentrated nitric acid, followed by cooling to crystallize the hydrate. Seeding with a small quantity of pure crystals is usually recommended, as there is a strong tendency to form supersaturated solutions.[1433]

Mercuric Sulfate. Mercuric sulfate is prepared by reacting a paste of freshly precipitated and washed yellow mercuric oxide with the calculated amount of sulfuric acid, followed by filtration of the white crystalline sulfate on a nutsch and subsequent drying.[1433] It may also be prepared by heating mercury with an excess of sulfuric acid; the formation is favored at high temperatures.[2039]

Mercuric Diammonium Chloride. Mercuric chloride diammine is made by dissolving mercuric chloride in a strong aqueous solution of ammonium chloride, and adding ammonia solution. It may also be prepared by treating finely powdered dry mercuric chloride with anhydrous ammonia vapor.[1433] The major U.S. producers of inorganic mercury chemicals include the following:[0637]

Allied Chemical Corp,; Specialty Chemicals Division; Morristown, New Jersey

City Chemical Corp.; Jersey City, New Jersey

Mallinckrodt Chemical Works, Industrial Chemical Division; Jersey City, New Jersey

Merck & Co., Inc., Merck Chemical Division, Rahway, New Jersey

Troy Chemical Corp.; Newark, New Jersey

Ventron Corp., Alfa Products; Beverly, Massachusetts

Ventron Corp., Chemicals Division; Beverly, Massachusetts

Uses

The U.S. demand for mercury can be broken down into recyclable and dissipative uses, which account for 74 and 26 percent of the total respectively. Recyclable uses are defined as those for which it is technically feasible to recycle, whereas for dissipative uses it is not.[2105]

The major use of mercury is as a cathode in the electrolytic preparation of chlorine and caustic soda. Actual consumption in this manufacturing process is small for each unit, although large quantities are required for new installations (10 percent of 1968 demand). Because of the many plants now in operation, however, the requirement to replace losses has become a major use (23 percent of 1968 demand). Large quantities of mercury are also used in electrical apparatus, in industrial and control instruments, and in general laboratory applications. These potentially recyclable uses of mercury are for fluorescent and high-pressure mercury lamps, arc rectifiers, mercury battery cells, switches, thermometers, barometers, diffusion pump, vacuum gage, and as a vibration clamper.[1433, 2105]

The largest dissipative use of mercury is for antifouling and mildewproofing paints. Mercury compounds are also widely used in agriculture as a result of their broad antifungal capabilities, for catalytic purposes, and formulated into many of the over-the-counter cosmetics (such as creams and lotions, hair preparations, and facial make-up) and patent medicines (antacids, astringents, eye drops, laxatives, nasal sprays, skin antiseptics, contraceptives). Mercury is used in dental amalgams, and to a decreasing extent, for the control of slime in the paper and pulp mills.[0533, 2105]

Individual figures of mercury consumption by uses from 1964 to 1968 have been compiled by the Bureau of Mines (Table 1), and indicate that about 2/3 of the total 1968 consumption was accounted for by four major use categories which have shown an increasing level of consumption over the 5-year period (Table 2). Declining levels of consumption were noted for industrial and control instruments, dental preparations, pharmaceuticals, and in paper and pulp manufacture (Tables 1 and 2).

An estimate of the current and future use pattern of mercury over the next 5-year period has been presented by Jones[0533] (Table 3). Of the eleven major categories represented, increasing demands are forecast in seven including catalysts, dental preparations, electrical apparatus, electrolytic preparation of chlorine and soda, industrial and control instruments, paints, and pharmaceuticals. General laboratory uses are expected to continue at about the same level, while decreasing levels of mercury consumption are indicated in agriculture, amalgams, and paper and pulp manufacture. These predicted trends in mercury consumption also points toward the direction where future efforts of mercury recovery and pollution control should be aimed.

Of the four inorganic mercury compounds included in this Profile Report, mercuric diammonium chloride is of no commercial significance; whereas mercuric chloride is one of the most industrially important mercury compounds. Mercuric chloride is used for the production of various mercuric compounds as a catalyst in vinyl chloride manufacture and other organic reactions, and as a preservative for wood. In agriculture, it is used either as a dust or spray for the control of certain fungus diseases on seeds. Solutions of mercuric chloride are used medicinally as an antiseptic, and in photography to intensify negatives.[1433]

Mercuric nitrate is used in the preparation of other mercury compounds, and in particular, mercury fulminate. It is also used in the manufacture of felt, and for the destruction of phylloxera.[0637]

Mercuric sulfate is mainly used as an electrolyte for primary batteries.[0637] Aside from its occasional use as a catalyst, mercuric sulfate has been employed in conjunction with sodium chloride to extract gold and silver from roasted pyrites.[1433]

Sources and Types of Waste

The wide variety of uses of mercury and mercury compounds by man has resulted in significant mercury pollution of the environment in many parts of the world. By far the single largest source of commercial discharges of mercury during 1968 was derived from inventory losses suffered by the chlor-alkali plants. Approximately 30 percent of the U.S. supply of chlorine comes from mercury cells, which produce a higher grade caustic soda that is highly concentrated and essentially free of chloride impurities, and thus the trend in new construction has greatly favored the mercury cell. The total chlorine capacity of mercury cells in the United States is about 8,000 tons per day from about 35 installations around the country, with plant capacities ranging from 20 to about 700 tons per day. In the mercury cell process, a circulating sodium chloride solution is electrolyzed in the cell in which mercury serves as the cathode; the anode is usually graphite. Sodium ion reacts with mercury to form an amalgam, and chlorine gas is produced at the anode. The mercury flows through the cell, picking up sodium on the way, and is pumped to a regeneration cell, where the amalgam is mixed with water and forms one-half of a self-shorted electrolytic cell, with iron serving as the other electrode. The regeneration cell removes sodium from the amalgam and produces caustic soda (approximately 50 percent solution) and hydrogen gas. The regenerated mercury is then returned to the mercury cell, and the process is repeated. The brine solution leaves the mercury cell and is vacuum de-chlorinated and then purged with air to remove the last of the chlorine. The solution is then saturated with salt, and this is followed by a purification step, in which various impurities from the newly added salt are precipitated. The brine is then passed through a filter and back to the mercury cell.

The primary sources of mercury loss in mercury-cell chlor-alkali plants are the hydrogen gas stream, the sludge from the brine purification process, the caustic soda stream, cell room ventilation air, and various waste wash water (Table 4).[0533, 2042, 2062, 2105] The reported values of mercury loss from Swedish and U.S. plants are 55 to 190 gm/ton and 202 to 538 gm/ton of chlorine produced respectively in 1968. As early as 1970, however, it was technically feasible to reduce the total mercury loss from a chlor-alkali plant to only 0.63 to 2.11 gm/ton of chlorine produced.

Based upon 1968 U.S. data, 17,424 flasks of mercury were used in the manufacture of chlorine, which represents an industry average of about 0.5 lb of mercury loss per ton of chlorine produced.[0533] However, this loss can apparently be decreased by one to two orders of magnitude by proper plant management. During the summer of 1970, lawsuit threats and tentative water standards caused many of the chlor-alkali manufacturers to reduce their mercury discharge significantly. As monitored by the Department of Interior, the overall level of mercury emission to receiving waters was found to be dropped 86 percent from 287 lb per day in July to 40 lb per day in September 1970.[2105]

Of the mercury used in 1968 for other potentially recyclable uses, such as electrical equipment, measurement and control apparatus, and general laboratory uses, 520 tons were recycled and 660 tons had an unknown disposition, (in batteries, fluorescent tubes, switches, etc.) and probably ended up mostly in landfills, dumps, and incinerators.[2105]

The dissipative uses of mercury include paints, agriculture, dental fillings, catalysts, paper and pulp manufacture, and pharmaceuticals; a total of 26 percent (745 tons) of the mercury demand in 1968. Mercury from these various uses enter the environment in a variety of ways and at different rates. For example, although mercury-formulated paints constitute a considerable source, their release into the environment is rather slow and probably has a minimal effect. Dental amalgams also apparently have no measurable effect on the user. On the other hand, mercury catalysts employed for acetaldehyde and vinyl chloride manufacture and mercury formulations used as seed dressings have promoted serious consequences, even though such usage represents a small percentage of the total consumption. However, in March 1970, the U.S. Department of Agriculture suspended 42 alkylmercury compounds from interstate commerce. Furthermore, the use of mercury compounds as slimicides in the paper and pulp industry has decreased drastically since the early 1960's so that it now amounts to well less than one percent of the total demand.[2105]

Other man-made sources of environmental mercury include mine tailings and vapor released by the mining and smelting of mercury, and a stack loss of three percent during the refining process would mean that 31 tons were emitted into the atmosphere from smelting during 1968. In addition, ore deposits of heavy metals are generally surrounded by aureoles in which a notable enrichment in mercury has occurred, and considerable mercury generally escapes from stacks during the smelting of tin, zinc, copper, and gold. As an example, zinc concentrates from Tennessee contain an average of 5 to 10 ppm mercury; thus a single smelter handling 500 tons per day might emit as much as 10 lb mercury vapor daily.[2105]

Another major source of airborne mercury is the combustion of paper products and fossil fuel. The actual amounts of mercury in fossil fuels are quite variable, but preliminary values for U.S. coals average from 0.5 to 3.3 ppm mercury.[2100] Since about 550 million tons of coal are burned in the United States every year, a conservative estimate of 1 ppm mercury in coal would correspond to an annual release of 550 tons of mercury to the environment. However, although the general consensus was that fly ash from coal-burning plants contained negligible amounts of mercury so that the mercury present in the coal must be released to the atmosphere during the combustion process, a recent U.S. Bureau of Mines study revealed that more than 70 percent of the mercury could be trapped by the fly ash (which can be separated out of the stack gases) and thus be more readily amenable to recovery.[2172] No information is available on the mercury released during petroleum processing and oil burning, although it is believed that the enormous amounts of these substances consumed and burned in the United States each year probably contribute a substantial amount to mercury pollution. Samples from California crudes have yielded mercury values in the range of 1.0 to 21 ppm; and related tars which have lost much of their volatile hydrocarbons are known to contain as much as 500 ppm mercury.[2117]

Lastly, because mercury has a tendency to vaporize and is widely distributed, mercury also enters into the environment through natural sources. The air over mercury ore deposits and precious metal or copper ore deposits generally contain elevated levels of mercury. Relatively high concentrations of mercury are also likely to occur in underground waters because of the longer and intimate contact with mineral grains. Oil field brines, hot springs, and geothermal stream fields have been associated with high mercury levels, and hot vapors which stream up through fine-grained muds produce mud volcanoes and deposit considerable quantities of mercury during condensation.[2117]

Physical and Chemical Properties

The physical and chemical properties of mercury and the four inorganic mercury compounds are summarized in the attached worksheets.

2. TOXICOLOGY

Inorganic mercury may enter into the body by adsorption through inhalation of elemental mercury vapor or aerosols of mercuric salts and by oral ingestion. Penetration through the skin, on the other hand, is rather slow.

Inhalation of mercury in concentrations of 1,200 to 8,500 micrograms per cubic meter in air results in acute intoxication, affecting primarily the digestive system and kidneys, and is characterized by a metallic taste, nausea, abdominal pain, vomiting, diarrhea, headache, and sometimes albuminuria. After a few days, the salivary glands swell, stomatitis and

and gingivitis develop, and a dark line of mercuric sulfide forms on the inflamed gums. Furthermore, teeth may loosen and ulcers may appear on the lips and cheeks. Severe exposure to mercury vapor produces tightness and pain in the chest, difficulty in breathing, and coughing. Severe cases of acute poisoning are characterized in later stages by hemolysis, sleeplessness, headache, facial tics, digital tremors, delirium and hallucinations. Death as a result of extreme exhaustion frequently occurs with poisoning of this degree of severity. In milder cases of acute mercury poisoning, some patients recover within 10 to 14 days, but others may develop the chronic symptoms, such as muscular tremors or erethism.[0637]

Chronic poisoning of mercury is more common than the acute form. In the case of chronic poisoning of inorganic mercury, symptoms and signs involving the central nervous system are most commonly seen, the principal features being tremors and psychological disturbances. Symptoms related to the mouth, such as gingivitis, stomatitis, and excessive salivation, may occur along with a number of nonspecific symptoms such as loss of appetite, weight loss, anemia, and muscular weakness. Intoxication from mercury vapor or from absorption of mercuric salts may be due, in both cases, to the action of the mercuric ion. Metallic mercury is able to diffuse much more extensively into the blood cells and various tissues than inorganic mercury, but once distributed, most of it is oxidized to the mercuric form. Numerous cases of industrial exposure to mercurials with resultant toxic symptoms have been reported, mostly involving incidents in the mining of hat-felt industries (which utilizes mercuric nitrate). In most cases, however, symptoms of mercury poisoning were observed only among workers who had been exposed to mercury levels above 100 micrograms per cubic meter in air.[2105]

It has been reported that a 1 gm oral dose of mercuric chloride could cause death in adults whereas a 0.1 gm dose would lead to chronic illness.[2117] The acute oral LD50 of mercuric chloride to rat is 37 mg/kg body weight, and that of mercuric nitrate to mouse is 4 mg/kg body weight.[1312]

The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended as Threshold Limit Values (TLV) for 1971 a time-weighed average concentration of 50 micrograms per cubic meter in air for metallic mercury vapor and inorganic mercury compounds.[0225] The new ACGIH TLV for inorganic mercury is probably based on the report of the 1968 International Symposium at the Karolinski Institute, Sweden, which recommended 8-hour Maximum Allowable Concentrations (MAC) of 50 micrograms per cubic meter in air for mercury vapor and 100 micrograms per cubic meter in air for inorganic mercury salts.[2036]

The lethal concentrations of mercury compounds for various aquatic organisms have been summarized in a 1970 U.S. Geological Survey Report.[2117] For mercuric chloride, the lethal concentrations in ppb for aquatic organisms are: Escherichia coli (bacteria), 200; Schenedismus (phytoplankton), 30; Microregma (protozoa), 150; Daphnia magna (zooplankton), 6; Marinogammarus marinus (amphipod), 100; Polycelis nigra (flatworm), 270; Bivalve larve (mollusca), 27; Australorbis glabratus (mollusca), 1,000; Stickleback (fish), 4 to 20; Guppy (fish), 20; Eel (fish) 27; Rainbow trout (fish), 9,200. For mercuric nitrate, the lethal concentrations in ppb for aquatic organisms are: Mesospheroma oregonensis (isopod), 15; Mercierella enigmatica (polychaete), 1,000; Stickleback (fish), 20; Guppy (fish), 20. No aquatic toxicity data are available for mercury, mercuric sulfate, or mercuric diammonium chloride, as mercuric sulfate decomposes in cold water into a yellow insoluble basic sulfate and free sulfuric acid, and both mercury and mercuric diammonium chloride are insoluble in cold water. It must be remembered, however, that mercury and all inorganic mercury compounds discharged into the aquatic environment could eventually be biologically converted into the more toxic methyl mercury by anaerobic microorganisms,[0658, 2099] which can then be concentrated through food chains to fish living in both fresh water and marine environments, thus leading to the present dimensions of the mercury pollution problem.

3. OTHER HAZARDS

All inorganic mercury compounds, with the notable exception of the halides, decompose to give toxic fumes of mercury on heating.

In addition to its toxic properties, mercuric nitrate also possesses some of the properties of nitrates. Acetylene forms a sensitive acetylide when passed into an aqueous solution of mercuric nitrate. Alcohols should not be mixed with mercuric nitrate, as explosive mercury fulminate may be formed. Reactions of mercuric nitrate and phosphine give a yellow precipitate, which explodes when heated or subjected to shock. Mercuric nitrate also reacts with unsaturates and aromatics with violence if given time to generate enough heat, and could lead to explosions in its use for determining sulfur in Ball's reaction.[0096]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Because of the extreme toxicity of mercury and mercury compounds, care must be exercised in their handling to minimize contact with the skin or the inhalation of airborne dust, as well as ingestion. Safety precautions should include adequate ventilation of all work and storage areas, enforcing strict standards of housekeeping and personal cleanliness, and the use of protective equipment. Workers should be examined periodically by competent physicians, and referred to medical treatment after any mishap that might give rise to an abnormally high intake of mercury.

The volatility of mercury and the dangers of airborne inorganic mercury salt dusts have necessitated the storage of mercury and inorganic compounds in tight containers. Mercury, mercuric chloride, and mercuric sulfate are classified as Poison B by the Department of Transportation (DOT), and the rules governing its transportation are given in the Code of Federal Regulations (CFR) Title 49--Transportation, Parts 100 to 199.[0278] Although mercuric nitrate and mercuric diammonium chloride are not on the DOT list of hazardous materials, the same regulations for Class B Poisons should also be applied in the transportation of these compounds because of their toxic nature.

Spilled mercury and inorganic mercury compounds on floors can normally by handled by several of the removal methods available. Sweeping with special vacuum cleaners can effectively remove large droplets of mercury and the greater portion of inorganic mercury salt in powder or dust form, and this can be followed by flooding with water, collection of the water with suction pumps, and subsequent removal of the mercury from the contaminated water by chemical precipitation, chemical reduction, ion exchange, or solvent extraction methods. For the chemical removal of mercury, a substance is generally applied to react readily with mercury at ambient temperatures forming nearly nonvolatile mercury compounds, which can then be swept up. The chemical agents commonly used are inorganic polysulfides or powdered sulfur.[0533]

Methods suggested for treating water spills of mercury and inorganic mercury compounds include adsorption with activated carbon and ion-exchanger masses such as the Q-13 resin. Results of experiments conducted at the Cornell Aeronautical Laboratory (CAL) has shown that an activated carbon dose of 500 ppm could effect greater than 99 percent removal of mercury from water with an initial mercury concentration (as mercuric chloride) of 100 ppm, and it has been suggested the activated carbon could best be introduced into the stream in water-permeable bags which would allow the pollutant-laden water to pass through the bag material and interact with the contained carbon.[1419] Ion-exchanger masses that could be employed in treating water spills of mercury will be discussed later along with other methods for removing mercury and inorganic mercury compounds from liquids.

Disposal/Reuse

The greater portion of mercury and inorganic mercury compounds present in air and water waste streams can be removed and the mercury recovered for its value. However, although zero mercury discharge is the eventual goal of all concerns, this is not achievable with current technology, especially when economical factors are also considered. For these reasons, the safe disposal of mercury and inorganic mercury compounds must still be defined in terms of the recommended maximum concentrations released to the atmosphere and a potable water source and/or marine habitat. These recommended maximum concentrations are as follows:

Contaminant and Environment	Maximum Allowable Concentration	Basis for Recommendation
Mercury and inorganic mercury compounds in air	1 microgram/cu. meter/24 hours	MAC in Germany; 0.02 ACGIH TLV
Mercury and inorganic mercury compounds in waste water discharged to aquatic environment	5 ppb	Federal drinking water regulation; lower limit attainable with current technology

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL/RECOVERY PROCESSES

Removal from Gases

Removal of mercury from gases usually concerns one of two types of operation. The first is removal of mercury vapor from the hydrogen produced in the mercury-cell chlor-alkali process. The second involves the more general problem of the removal of mercury vapor from gases such as air, incineration effluents, and natural gas.

Hydrogen produced by the electrolysis of brine at a mercury cathode contains substantial quantities of mercury vapor, at times more than 20,000 micrograms of mercury per cubic meter, and is usually saturated with water vapor. It is desirable to substantially lower the mercury concentrations in hydrogen, not only from the environmental standpoint, but also because the presence of mercury at concentrations higher than 10 micrograms per cubic meter interfere with the use of hydrogen in catalylic reductions of organic compounds.[0537] The common current practice is to remove the greater portion of the mercury present by initially cooling the hot hydrogen gas stream (80-120 C) to 5 C before it is sent through other gas treatment systems.[2047] The equilibrium concentration of mercury in the gas phase changes dramatically with temperature. A reduction in temperature to 5 C from 80 C will bring the equilibrium concentration in the hydrogen gas stream down to 3.7 mg per cubic meter from 565 mg per cubic meter.[2062]

The removal of mercury vapor from air and other gases is obviously desirable for health reasons. Health hazards exist if the concentration of mercury vapor in air rises above the recommended MAC in chemical laboratories where mercury is used or in plants, such as those utilizing mercury boilers and leakage of mercury vapor may possibly occur accidentally. Dangerous concentration may also readily exist in enclosed places due to exposed or spilled liquid mercury as air saturated with mercury vapor at ordinary temperatures may contain around 0.015 gm of mercury per cubic meter, far exceeding the safe level.

The several methods available for the removal of mercury from gas streams are discussed below.

Option No. 1 - Removal with Mist Eliminators. The Brink mist eliminators developed by the Monsanto Enviro-Chem Systems are being used by many U.S. chlorine plants, and have been tested over a period of several months by Georgia-Pacific at its Billingham, Washington plant as part of that company's overall program to cut mercury emissions, with highly successful results.[2047, 2062] The hydrogen gas stream containing an equilibrium mercury concentration of 3.7 mg per cubic meter is sent through the Brink mist eliminators, which are fiber beds packed between two flat parallel screens or between concentric cylindrical screens, and 90 to 95 percent of the particulate mercury are removed in a readily recoverable form. A similar type of filter separators consisting of coalescing filter elements preceding a mist eliminator has also been recently installed in well clusters to extract the major portion of the mercury produced with Dutch natural gas by NAM, the Netherlands producing company and operator of the giant Groningen gas field.[2049] The mercury content of the Groningen gas at the wellhead is 180 micrograms per cubic meter, and the gas is first cooled by air and then further cooled to -12 C by Joule-Kelvin expansion. Much of the mercury in the gas condenses with the water and hydrocarbons and is drawn off with the condensate, and in the process the mercury content of the gas discharged from the coolers is reduced to about 40 micrograms per cubic meter. The tiny droplets of mercury carried in the gas are then removed efficiently by passing the cooled gas through the coalescing filter separators, so it is insured that the gas entering the transportation network contains no more than 12 micrograms per cubic meter of mercury. Although both the Brink mist eliminator and the NAM coalescing filter separator do not reduce the mercury concentration in the gas stream to the recommended MAC level, a second stage unit could be added to remove the last remaining traces of mercury. For example, Farbenfabriken Bayer has a catalytic approach capable of reducing the mercury level to less than 1 microgram per cubic meter and would be ideally suited for this purpose.[2047]

Option No. 2 - Adsorption with Molecular Sieves. Although the use of molecular sieves for the removal of mercury vapor from hydrogen has been investigated by Logan as early as 1966, it was found that the Union Carbide Type 13X molecular sieve employed in the study had a very low capacity for mercury.[2050] However, a process called PuraSiv Hg that utilizes a new type of proprietary molecular sieves has recently been developed and marketed by Union Carbide's Molecular Sieve Department, and a commercial unit (outside of Union Carbide) is presently being put on-stream at Sobin Chlor-Alkali's Orrington, Maine chlorine plant.[2104] The PuraSiv Hg Process can be applied to any mercury containing gas stream, and consists of three separate skids mounted in tandem: (1) a blower skid; (2) a chiller/demister skid; and (3) an adsorption skid. In a typical PuraSiv Hg unit (Figure 1), the hydrogen gas stream at atmospheric pressure (evolving from the chlorine plant decomposer system) and containing 10 ppmv mercury first enters the PuraSiv Hg blower skid, where its pressure is increased by 4 to 5 psi. The compressed gas next passes through the knock-out pot into the chiller/demister skid, which consists of a packed chiller unit, a chilled water heat exchanger, and a Petersen separator. As the hydrogen cools, water and elemental mercury mists are formed, and these mists are removed in the Petersen separator and recycled to the chlorine plant as a liquid stream. The separator itself consists of stacks (or candles) of ring elements specially contoured to act as converging-diverging nozzles, and the mist particles collect on the diverging side of the rings and are washed away with spray water. The low mist content hydrogen leaves the separator and enters the adsorption skid, which consists of two adsorber vessels and auxiliary equipment. Gas enters the "on-line" vessel (while the other bed is being regenerated) and flows upward through the bed of PuraSiv Hg adsorbents so that the remaining mercury is trapped. During the first 20 hours of operation, essentially no mercury breaks through the adsorbent bed. In the remaining 4 hours of the run, however, the effluent concentration increases gradually to 50 ppbv. Commercial PuraSiv Hg Systems are designed to be regenerated every 24 hours by heating a portion of the effluent gas in an electric furnace and passing it downward through the vessel, thus stripping out the mercury. The relatively concentrated mercury stream is then recycled through a water cooled heat exchanger, a knock-out pot, and into the suction of the blower, with final recovery of the stripped-out mercury occuring in the demister. PuraSiv Hg Systems are guaranteed to provide effluent mercury levels averaging less than 60 ppbv for 3 years, so that the total mercury emitted with the effluent hydrogen from a 300 ton per day chlorine plant will be less than 0.1 lb per day and below the proposed Federal Standards for total mercury emission.* This guaranteed mercury level of 60 ppbv (540 micrograms per cubic meter), however, is considerably above the level of any acceptable environmental standard for mercury in air or the permissible level of mercury in hydrogen for industrial uses. To render the Union Carbide PuraSiv Hg System useful for a wider range of applications, it is suggested that either the bed volume of the adsorption vessels be increased or a shorter on-line time for the adsorption vessels be instituted (this can be accomplished by installing more adsorption vessels if a regeneration time of 24 hours is required), so that the level of mercury in the effluent from the adsorbent bed will remain extremely low (below 1 ppbv) at all times.

Option No. 3 - Adsorption with Activated Carbon. Although activated carbon by itself is a relatively inefficient adsorbent for mercury, its adsorption capacity for mercury can be greatly enhanced by impregnation with silver, potassium iodide, or any other substance that will react with mercury.[2065, 2066, 2068] However, as only in some instances (such as adsorption on silver) can the substrate be regenerated by heating to around 400 C, adsorption with mercury reactant impregnated activated carbon has not received wide acceptance in the industry. In addition to the difficulty of adsorbent regeneration, the process is also too expensive and its efficiency may be drastically reduced by the presence of water.

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*Proposed Federal Standards for Chlorine plants allow 1,000 gm (2.2 lb) per day of mercury in the by-product hydrogen and seal air streams (combined total).

Option No. 4 - Scrubbing with Oxidizing Solutions. A fourth approach in removing mercury from gases consists of adsorption with a strongly oxidizing aqueous solution so as to bring the mercury into solution in the mercuric state; the mercuric ions can then be removed from solution by methods such as chemical precipitation, chemical reduction, ion exchange, or solvent extraction.[2062] Although an acid permanganate solution can be used for this purpose in the same fashion as is done for the analytical determination of mercury, the introduction of a completely foreign stream into the system and subsequent recovery of the metal from the loaded solution will require an additional processing system. A more attractive alternative, therefore, is to use sodium hypochlorite as the oxidizing agent. Sodium hypochlorite had been used already for a few processes where hydrogen had to be purified for use in the preparation of hydrogenated fats or foodstuffs, or in catalytic reactions where the catalyst was subject to mercury poisoning.[2064, 2069] The hypochlorite system has been installed recently by at least one chlor-alkali plant for mercury removal and found to be highly effective.[2062]

Other processes for the removal of mercury from gas streams that have been investigated include adsorption with chromic acid on silica gel,[2050] adsorption with mercury-wettable materials on extended surfaces,[2085] adsorption with fused alumina oxide containing silver,[2067] and absorption with a suspension of manganese dioxide.[2042] Chromic acid on silica gel has a reasonably high capacity for mercury, but this could be significantly reduced by the presence of water vapor, presumably due to the strong physical adsorption of water molecules on the gel preventing access to mercury. In the case of adsorption with mercury-wettable materials on extended surfaces (such as fused alumina oxide), the preferred deposited adsorbent metal based on affinity for mercury is silver, which has the disadvantage of being easily poisoned by hydrogen sulfide or chlorine in the atmosphere. Application of the method on the commercial scale also remains to be demonstrated. Bench-scale tests have shown that mercury could be removed from gas streams by adsorption in a suspension of manganese dioxide, but again the process proved unsuitable for scale-up to the size of commercial units.[2049] These processes are therefore considered as inadequate methods for the removal of mercury from gas streams.

Removal from Liquids

Various liquid streams in the mercury-cell chlorine plant contain high concentrations of mercury which must be removed before they could be discharged to public waters. Depleted brine and the brine sludge formed on the subsequent treatment with soda and barium chloride are rich in mercuric ions, mostly in the form of the tetrachloro complex ($HgCl_4^{2-}$), and mercury can enter the aquatic environment when either a small portion of the depleted brine is bled off to prevent continual build-up of sulfate (originally present in the sodium chloride) concentration in the salt solution or through dewatering of the brine sludges. The cell room and caustic wash water and other aqueous solutions that are a part of mercury cell operations also contain soluble or colloidal mercury, primarily in the elemental form.

Other liquid streams containing inorganic mercury requiring treatment include: (1) wastewaters from manufacturers of mercury chemicals, chemcial plants using mercury catalysts, and paper and pulp mills using sodium hydroxide with a trace of mercury; (2) scrubbing solutions for removing mercury from gases; (3) leaching solutions for extracting mercury from ores, sludges and fly ash from combustion of fossil fuels; and possibly (4) sewage treatment plant effluents as a result of breakage of mercury seals used in trickling filters, switches, flow meters, and other instrumentation.

Several methods available for the removal of inorganic mercury from liquids are discussed below.

Option No. 1 - Chemical Precipitation. Inorganic mercury can generally be removed from liquid solution by direct precipitation as an insoluble metal salt either with or without further processing. Raising the pH to the range of 10 to 12 with sodium hydroxide or sodium hypochlorite will render mercuric oxide, which can then be removed by filtration.[2069] Mercury and mercuric ions could also be precipitated as mercuric sulfide by the addition of a soluble sulfide or hydrogen sulfide gas to the liquid solution.[2042, 2069, 2070, 2072] Sodium sulfide is generally used, and the colloidal mercuric sulfide formed could be separated from the liquid stream through flocculation with ferric chloride. Both these methods, however, suffer from the fact that precipitation is seldom complete (effluent often contains 1 ppm mercury) and the fine precipitate formed is difficult to remove.

Option No. 2 - Chemical Reduction. Mercuric ion can be chemically reduced from various liquid solutions with a variety of agents: alkali metals, zinc, antimony, iron, aldehydes, hydrazine hydrate, and sodium borohydride among many others. Direct reduction of mercuric ions by passing the waste stream and an alkali metal amalgam through either an active bed of amalgamated steel turnings and pieces or an inert bed whereby additional amalgam is obtained along with metallic mercury appears to be a unique and clean way of recovering mercury, but tests so far have indicated that a relatively high level of mercuric ions remain in the treated effluent.[2072, 2073] One set of results showed that the mercury content was reduced from 15.4 ppm to 3.3 ppm in the "active-bed" treatment and from 10 ppm to 7.2 ppm in the "inert-bed" treatment. Town described a method of precipitating elemental mercury from an aqueous sodium sulfide-sodium hydroxide solution containing mercury by the addition of elemental antimony,[2080] but an excess of antimony is usually required and the amount of mercury left in solution has not been analyzed. Niepert and Bon suggested the addition of an aldehyde to waste streams containing mercury compounds and the recovery of the reduced metallic mercury by settling.[2071] The method again proves to be unsatisfactory because of the high mercury concentration (approximately 1 ppm) remaining in the waste stream after treatment. However, two other chemical reduction schemes, the Ventron sodium borohydride process and the use of zinc dusts, appear to be able to improve wastewaters to low ppb mercury limits.

The Ventron Process.[1145, 2057, 2058] Sodium borohydride is a powerful reducing agent capable of reducing both mercuric and mercurous ions to the metal almost instantaneously. The reaction also has the advantages of taking place at low temperatures and is not critically pH dependent. In the Ventron flow scheme (Figure 2) wastewater containing inorganic mercury compounds is fed with a 12 percent solution of sodium borohydride (in 40 percent caustic soda) into a static mixer. The pH is held between 9 and 11. The hydride reduces the mercury compounds, yielding metallic mercury precipitate and hydrogen gas. Following separation of the gas, which is scrubbed with a dilute nitric acid solution to eliminate any mercury vapor, the slurry is passed to a cyclone. There 80 to 90 percent of the mercury comes out as a sludge. The clarified effluent is then sent to polishing filters where just about all of the remaining mercury is removed; the recovered metal is purified by vacuum distillation. A Ventron sodium borohydride unit has been onstream since January 1971 at its Woodridge, New Jersey mercury chemicals manufacturing facility. The waste treatment system presently handles 15,000 gallons per day of an effluent averaging 100 ppm soluble mercury. Experience with actual operation has indicated that effluent discharge from the Ventron system, after final polishing with activated carbon followed by chelating resins, contains less than 5 ppb mercury.

Zinc Reduction.[2060, 2074] Removal of mercury compounds from an aqueous solution having a pH between 7 and 11 and containing 1 to 500 ppm of dissolved mercury by contacting a bed of reductor metal (zinc or iron) has been previously described by Gilbert and Rallis. Mercury is recovered as the metal and the typical removal efficiency is 90 percent. More recently, the New Jersey Zinc Company (NJZ) has issued a report discussing the use of zinc to remove mercury from wastewater, including a summary of the results obtained by NJZ researchers. As described by NJZ, the simplest mercury removal method is to add an excess of fine zinc dusts and to keep the dusts suspended in the solution by constant stirring. The tanks and stirring blades should be baffled to avoid the formation of an air vortex, which would result in oxidation and loss of the metallic zinc. The excess zinc will quickly settle to the bottom of the bank when the agitation stopped. The tank effluent usually still contains a few ppm of zinc, but zinc is much less toxic to aquatic life and may even act as a desirable ecological nutrient. The metallic mercury obtained by zinc reduction could be removed by filtration. A method more applicable to the treatment of industrial wastewater, however, is to pass the streams containing mercuric ions through a bed of coarser commercial zinc powders. The metallic mercury forms an alloy with zinc in the bed, which could be recovered later by heating the crude alloy, distilling off the mercury, then condensing the vapors. In the NJZ laboratory investigations, solutions containing 10,000 ppb of mercury (prepared from either mercuric chloride or phenylmercury acetate) were purified to 20 ppb in 13 seconds, and to 5 ppb in 110 seconds, by passing them through a 4.7 in. deep bed of granular zinc with average particle diameters of 2 mm. A slightly deeper bed lowered the mercury concentration from 10,000 ppb to 2 ppb in 60 seconds. The treatment is generally effective for streams within a pH range of 5 to 10.

Option No. 3 - Ion Exchange. Ion exchange is another effective method for removing mercury from liquids. Through the process of adsorbing mercury on a resin and then eluting it during regeneration, a harmful substance is removed from a waste stream and transferred to another more concentrated solution where it can be easily precipitated by conventional techniques. A few cation exchangers have been reported to be quite successful in extracting ionic mercury, including the Dowex 500W X-8, the Dowex A1, and the Amberlite IRC-50.[2052] Chuveleva et al[2051] made studies with the carboxylic acid resin SG-1 on mercuric nitrate solution, taking advantage of the stability of the acetate - Hg(II) complex. Cation-exchange resins, however, have no application in brines where, because of the high chloride concentration, mercury exists as the $HgCl_4^{2-}$ anion. Most successful ion exchange processes for the removal of mercury from liquid, therefore, employ either anion-exchange or chelating resins. A number of patents exist describing the use of quaternary ammonium cross-linked resins. Calkins et al discussed the selective removal of mercuric ions from brines containing halide ions and metal ions, with an insoluble homopolymer or copolymer prepared from at least one monomer of the group consisting of vinyphenyl aliphatic primary and secondary aminomonocarboxylic acids and mixtures containing a predominant amount by weight of at least one such aminomonocarboxylic acid and a minor portion of divinylbenzene.[2075] As an example, the effluent brine initially containing 15 ppm of mercuric ions, after passage through a bed of a copolymer of vinylphenyl glycine and N,N-bis (vinylbenzyl) glycine was found to contain 0.3 ppm of mercuric ions, and mercury was recovered from the resin bed by elution with sodium chloride solution at pH7. Both the Schotten and Prielipp patent[2076] and the Crain and Justice patent[2079] discussed the use of a strongly basic anion-exchange resin of insoluble quaternary ammonium composition to remove mercuric ions from liquid solution, with typical effluent mercury concentration less than 0.01 ppm, and regeneration of the ion-exchange resins with aqueous sulfide solution. Of the commercially developed ion-exchange resins, the Amberlite IRA-400 has been shown to adsorb significant quantities of mercury regardless of pH as long as it is present as an anion.[1795] Two other proven processes in commercial operation, however, are applicable to most mercury-bearing streams found in the industry. Both the Osaka Soda Process and the Aktiebolaget Billingsfors-Langed Process also have the ability to reduce the mercury content in wastewater to less than 5 ppb, and are discussed in greater detail below.

The Osaka Soda Process.[1145, 2045, 2061] In the Osaka Soda Process (Figure 3), wastewater is first collected in a storage tank, where any metallic mercury present is allowed to settle out. It is then chemically treated for adjustment of pH and free-chlorine concentration (if necessary), followed by filtering to remove any floating insolubles. The filtered water is passed through a tower packed with Osaka Soda's proprietary ion-exchange resin (IE), and the mercury content of the wastewater is reduced to a range of 100 to 150 ppb. Next, the waste stream passes through a tower packed with another Osaka Soda's proprietary resin, designated "MR". Mercury content is reduced to an undetectable level in the MR tower when a fresh charge is provided, although the effluent concentration gradually builds up to 5 ppb and is typically 2 ppb. Mercury values are recovered from the ion exchanges by periodic stripping. A sodium amalgam or other agent is then added to the pregnant stripping liquid to reduce the mercury to metallic form. Generally, IE resin beds are regenerated approximately once a week, whereas the MR resin is simply discarded several times a year after recovery of the mercury. Five Japanese chlor-alkali plants, ranging in capacity from 70 to 200 tons per day, have been using the Osaka Soda process for six years, treating 18,000 to 32,000 gal per day of wastewater. It should be noted, however, that caustic-soda-bearing streams cannot be treated by this process because of the poisonous effects of the caustic on the IE resin. Also, the IE resin cannot handle sulfides, but since naturally occurring hydrogen sulfide reacts with mercury and precipitates prior to introduction to the treatment plant, this limitation is not expected to be a problem. The process is licensed in the United States by Crawford and Russel.

The Aktiebolaget Billingsfors-Langed Process.[1144] In this Swedish developed process (Figure 4), which has been in operation for two years, wastewater is first passed to a vessel where the pH is adjusted to between 5 and 7 and metallic mercury in colloidal form is oxidized by chlorination. Since the resins subsequently used are sensitive to oxidizers, excess chlorine is removed in a dechlorinator via acitvated-carbon filtration. The water is then piped to a series of ion-exchange towers filled with a special, stable resin, dubbed Q-13. Mercury level is cut to around 100 ppb. No chloride ions are needed for good performance. The mercury level is reduced to a few parts per billion in an absorption tower containing another resin, called Q-Sorb. The Q-13 resin is regenerable, and yields an eluate rich in mercury. This can be passed to an electrolytic circuit for recovery of the metal. The Q-Sorb, however, is not regenerable by stripping. Although the composition of the Q-13 resin is proprietary, it is probable that this is the same ion-exchange resin described by Fuxelius and prepared from the reaction of sulfate pulp black liquor and epichlorohydrin.[2084]

Option No. 4 - Solvent Extraction. Chapman and Caban of the University of Wisconsin have recently developed a solvent extraction process for removing mercury from liquid or solid mercury-containing wastes, as well as crushed mercury ore.[2062] Mercury content in the feed is first converted to mercuric chloride, and the pH of the solution is adjusted to less than 3.0 by the addition of excess hydrochloric acid. The liquid waste stream is then brought into contact with a xylene phase that contains tri-iso-octylamine (TIOA), so that the mercuric chloride reacts with the amine, thus entering the xylene phase. The solubilities of both TIOA and TIOA salts in water are negligible, and a multistage countercurrent contacting system could be designed to remove almost all the mercury from the aqueous waste stream. For example, the mercury level in a depleted brine,originally containing mercuric chloride in concentrations of about 10 ppm Hg,can be reduced to 10 ppb by extraction with 0.1M TIOA in xylene after only six theoretical equilibrium stages. With an organic aqueous volume ratio of 0.01, an organic phase concentration of 1000 micrograms per multiliter mercury is obtained. In turn, the organic phase can be stripped of nearly all its mercury content with a small volume of brine at an equilibrium pH from 9 to 13. Again, this could be accomplished by the addition of enough sodium hydroxide to neutralize the hydrochloric acid in amine and bring the equilibrium pH to the desired value. By using a high organic to aqueous phase volume ratio, a resulting aqueous phase up to 10,000 times more concentrated in mercury can thus be obtained. Such concentrated solutions can undergo further processing more easily, both from a technical and economic viewpoint.

Option No. 5 - Filtration. Diatomite filtration is used to remove the insoluble mercury particulate matter that do not normally settle out by conventional treatment methods, and has reduced the mercury content of certain industrial wastes from a high of 5 ppm to less than 0.5 ppm. If the mercury is soluble, the waste stream is first chemically treated to convert the mercury to an insoluble form, such as elemental mercury, mercuric oxide, or mercuric sulfide.[2048] A more direct approach, however, is the Ecotech process currently under development that employs a filter medium of inorganic mineral containing magnesium.[2041] Mercury in any ionic form is directly reduced to elemental mercury in the filter medium by a replacement reaction, so that removal of soluble inorganic mercury from wastewater could be accomplished in a single step. Preliminary work at Ecotech has shown that: (1) for influent mercury concentration of 5 ppm or less, the removal efficiency in a single pass is typically 85 to 90 percent; (2) typical filtration rates are 2 to 4 gal per sq ft per min; and (3) a minimum bed depth of 36 in. is normally required for single-pass treatment. According to Ecotech, the process is best suited for removing trace elements of mercury from large volumes of wastewater, such as the paper and Kraft mill effluents.

Option No. 6 - Chemical Absorption. The application of chemical absorbents for removing mercury from wastewater has been studied by Environmental Engineering.[1145] Laboratory and pilot plant data with a proprietary absorbent have demonstrated that concentrations of mercury contaminants can be reduced in minutes from 2,000 ppm to 50 ppb, and even lower levels may be possible.

Option No. 7 - Adsorption with Activated Carbon. The use of activated carbon for removing mercury from wastewater has been investigated by Ziegler and Lafornara,[1419] and their experimental results showed that a carbon dose of 500 ppm could effectively reduce the mercury concentration in water from 100 ppm (as mercuric chloride) to less than 1 ppm. MacMillan proposed a mercury removal system comprising of a bed of activated carbon sandwiched between nickel* and mesh pads, and reported that the mercury content of a mercury cell caustic soda liquor was reduced from 0.8 ppm at the beginning to 0.1 ppm after passing through the carbon-nickel bed.[2082] In both cases, however, the mercury concentration in the treated effluent is still considerably above the recommended level.

Removal from Solids

For the extraction of mercury from solids or semi-solids such as brine sludges and mercury catalysts, the general proposed procedure is to use sodium hypochlorite as the leaching solution. Adequate systems based on hypochlorite leaching or any other method to treat brine sludges containing traces of mercury, however, have apparently not been designed and placed into operation. For example, the brine sludges produced at Georgia-Pacific's Bellingham, Washington plant are currently being pumped into a small settling basin awaiting the development and installation of adequate treatment processes. In addition to hypochlorite leaching, another process has been recently proposed for the recovery of mercury from brine sludges or other solids. Yamori et al suggested dissolving the sludge in aqueous acid and then adsorbing the mercury content of the resultant solution on an anion exchange resin, from which the mercury can be eluted, preferably with hydrochloric acid, and recovered from the resultant elute.[2083] No quantitative data, however, was presented to allow evaluation of the process.

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*Nickel is wettable by mercury and resistant to attack by caustic soda.

To summarize, the adequate methods for removing mercury from gases are: (1) the Brink mist eliminator or the NAM coalescing filter separator, with a second-stage unit such as the Farbenfabriken Bayer catalytic system to remove the last remaining traces; (2) the Union Carbide PuraSiv Hg System; and (3) scrubbing with sodium hypochlorite solution.

The adequate methods for removing mercury from liquids are: (1) the Ventron sodium borohydride process; (2) chemical reduction with a granular zinc bed; (3) the Osaka Soda ion-exchange process; and (4) the Aktiebolaget Bellingsfors-Langed ion-exchange process. In addition, the Chapman-Caban solvent extraction process also shows considerable promise as a near future method for treating mercury containing liquid wastes.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Most of the mercury containing wastes generated by the industry, such as wastewaters from mercury-cell chlor-alkali plants, could best be handled and treated at the site of generation. There are, however, other types of mercury wastes where no simple adequate disposal/recovery methods exist, and these are probably prime candidates for National Disposal: brine sludges, poisoned mercury catalysts, mercury battery cells, mercury pesticide wastes, mercury paints, and possibly fly ash from coal and other fossil fuel burning power plants. Methods for the treatment of the mercury containing wastes at National Disposal Sites will include incineration and liquid extraction facilities, followed subsequently by recovery/removal of the mercury from the gas and liquid streams. For the recovery/removal of mercury from gases, the recommended processes are:

Process	Order of Preference	Remarks
Union Carbide PuraSiv Hg system	First choice	Demonstrated technology; simplicity in operation; no second-stage unit required for additional treatment of effluent.
Sodium hypochlorite scrubbing	Second choice	Demonstrated technology; insufficient pilot plant and full scale operating data for optimal design of scrubbing system.

For the recovery/removal of mercury from liquids, the recommended processes are:

Process	Order of Preference	Remarks
Aktiebolaget Billingsfors-Langed ion exchange process	First choice	In full scale operation for two years; ability to treat wastewaters containing mercury in any form; ion exchange resins not poisoned by caustic or sulfides.
Ventron sodium borohydride process	Second choice	Demonstrated technology; not critically pH dependent; requires final polishing of effluent with activated carbon or chelating resin; process applicable to wastewaters containing mercury ions rather than elemental mercury.

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HAZARDOUS WASTES PROPERTIES WORKSHEET

H.M. 253

H. M. Name Mercuric Chloride

IUC Name

Common Names corrosive sublimate

Structural Formula

$HgCl_2$

Molecular Wt. 271.50(1) Melting Pt. 276 C(1) Boiling Pt. 302 C(1)

Density (Condensed) 5.440 @ 25 C(1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

1 mm @ 136.2 C(2) 10 mm @ 180.2 C(2) 100 mm @ 237 C(2)

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 6.9g/100cc at 20 C(1) Hot Water 48g/100cc at 100 C(1) Ethanol soluble(1)

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison B(3) Coast Guard Classification

Comments White crystals or powder. Highly toxic.

References (1) 1570
(2) 1673
(3) 278

HAZARDOUS WASTES PROPERTIES WORKSHEET

H.M. 255

H. M. Name Mercuric Nitrate

IUC Name

Common Names

Structural Formula

$Hg(NO_3)_2 \cdot 1/2H_2O$

Molecular Wt. 333.61(1) Melting Pt. 79 C(1) Boiling Pt. decomposes(1)

Density (Condensed) 4.39(1) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water very soluble(1) Hot Water decomposes(1) Ethanol insoluble(1)

Others: visible in HNO_3, NH_3, acetone(1)

Acid, Base Properties

Highly Reactive with alcohols to form explosive mercury fulminate with acetylene to form a sensitive acetylide, and with unsaturates and aromatics(2)

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments White yellowish, deliquescent powder. Highly toxic.

References (1) 1570
(2) 0096
(3)

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H.M. 255

H. M. Name Mercuric Nitrate

IUC Name ______________

Common Names ______________

Structural Formula

$Hg(NO_3)_2 \cdot H_2O$

Molecular Wt. 342.61 Melting Pt. ______ Boiling Pt. ______

Density (Condensed) 4.3 @ ____ ____ Density (gas) ______ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

______ @ ______ ______ @ ______ ______ @ ______

Flash Point ______ Autoignition Temp. ______

Flammability Limits in Air (wt %) Lower ______ Upper ______

Explosive Limits in Air (wt. %) Lower ______ Upper ______

Solubility

Cold Water soluble Hot Water ______ Ethanol insoluble

Others: soluble in HNO_3

Acid, Base Properties ______________

Highly Reactive with ______________

Compatible with ______________

Shipped in ______________

ICC Classification ______________ Coast Guard Classification ______________

Comments Colorless crystal or white powder, deliquescent

References (1) 1570

(2)

(3)

H.M. 256

**HAZARDOUS WASTES PROPERTIES
WORKSHEET**

H. M. Name Mercuric Sulfate

IUC Name

Common Names

Structural Formula

$HgSO_4$

Molecular Wt. 296.65 Melting Pt. decomposes Boiling Pt.

Density (Condensed) 6.47 @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water decomposes Hot Water Ethanol insoluble

Others: soluble in acids

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison B(2) Coast Guard Classification Poison B

Comments White, crystalline powder. Highly toxic.

References (1) 1570
(2) 0278
(3)

H.M. 257

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Mercury

IUC Name

Common Names quick silver

Structural Formula

Hg

Molecular Wt. 200.59(1) Melting Pt. -38.9 C(1) Boiling Pt. 356.6 C(1)

Density (Condensed) 13.594 @ 20 C(1) Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

1.2×10^{-3} mm @ 20 C(1) 1 mm @ 126.2 C(3) 10 mm @ 184 C(3)

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 20-30 ppm in deaerated water Hot Water Ethanol

Others:

Acid, Base Properties

Highly Reactive with halogens, hydrogen, sulfide, sulfur, vapor

Compatible with

Shipped in

ICC Classification Poison B(2) Coast Guard Classification

Comments

References (1) 2105
(2) 278
(3) 1673

H.M. 503

**HAZARDOUS WASTES PROPERTIES
WORKSHEET**

H. M. Name Mercuric Diammonium Chloride

IUC Name Mercuric Chloride diammine

Common Names Fusible white precipitate

Structural Formula

$Hg(NH_3)_2Cl_2$

Molecular Wt. 305.56 Melting Pt. 300 C Boiling Pt.

Density (Condensed) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble Hot Water decomposes Ethanol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Poison B(2) Coast Guard Classification

Comments Rhombic crystal

References (1) 1570
(2) 0278
(3)

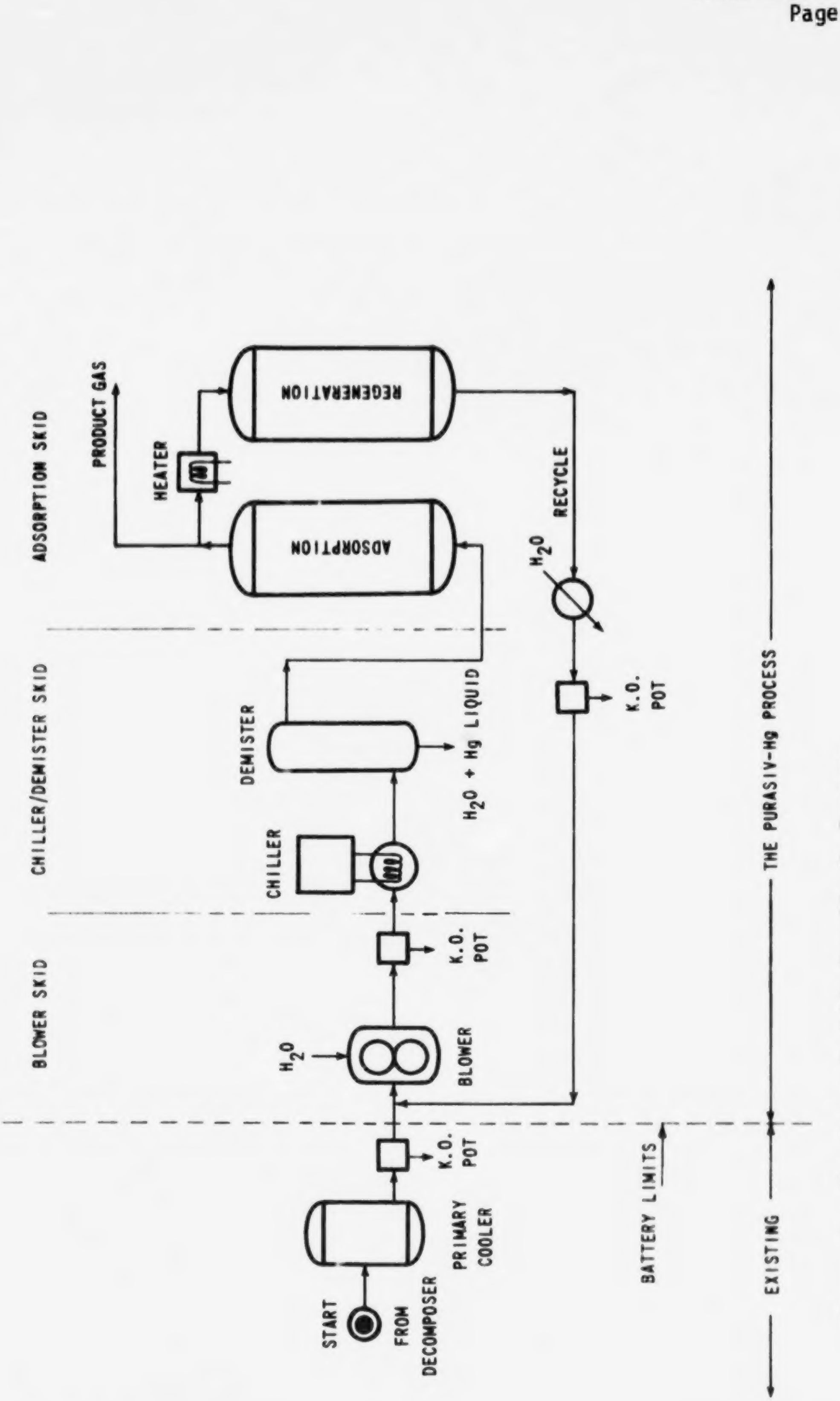

Figure 1. The Union Carbide PuraSiv Hg Process

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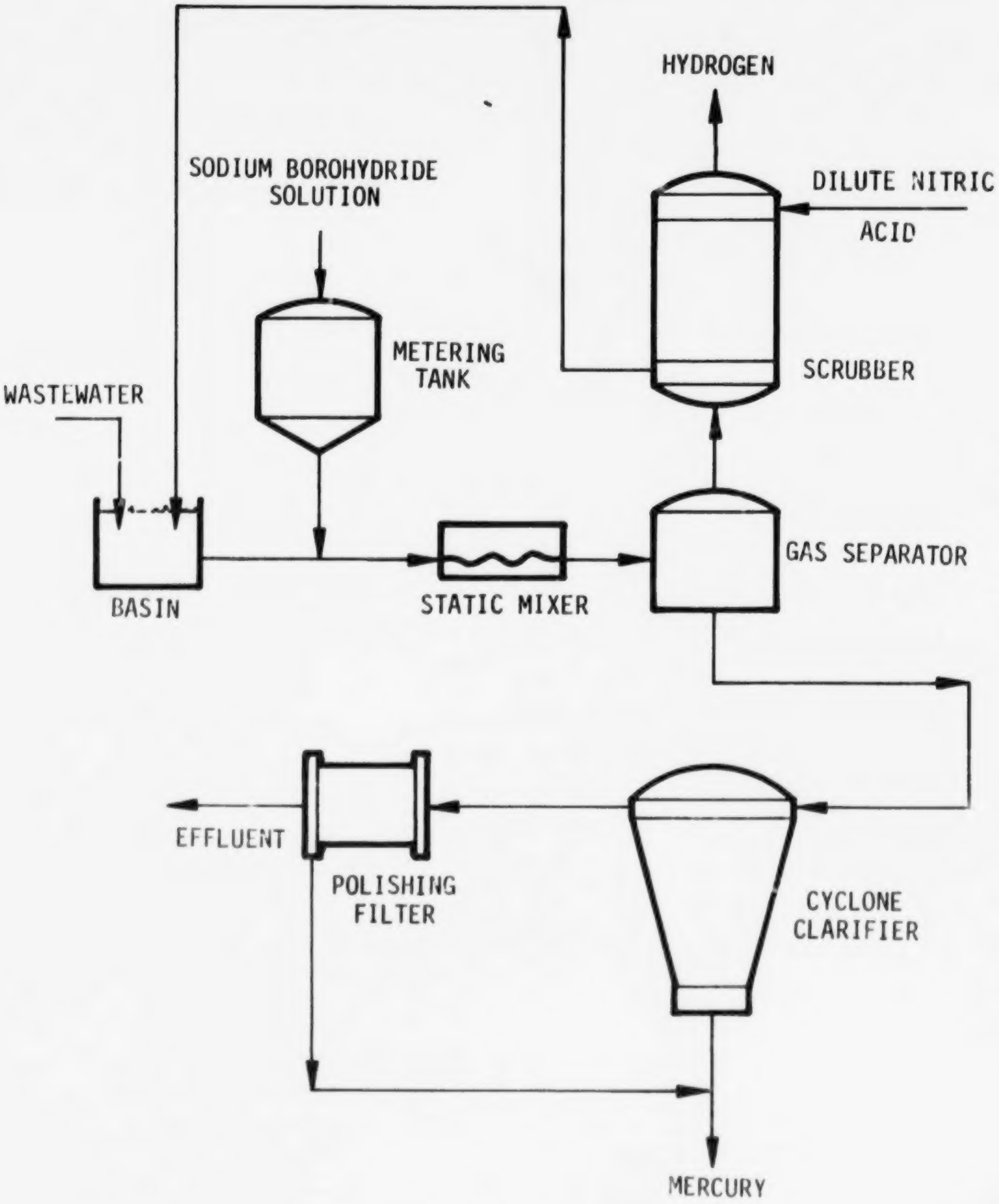

Figure 2. The Ventron Sodium Borohydride Process

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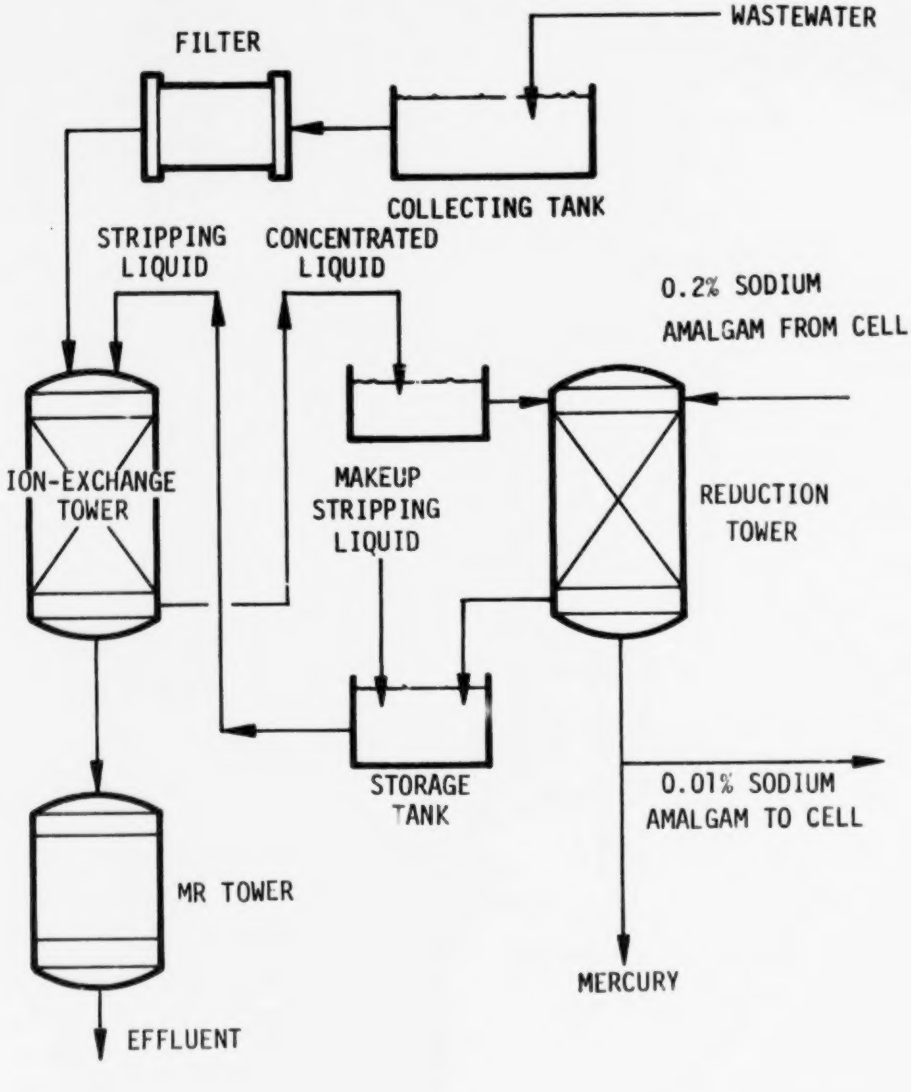

Figure 3. The Osaka Soda Mercury Removal Process

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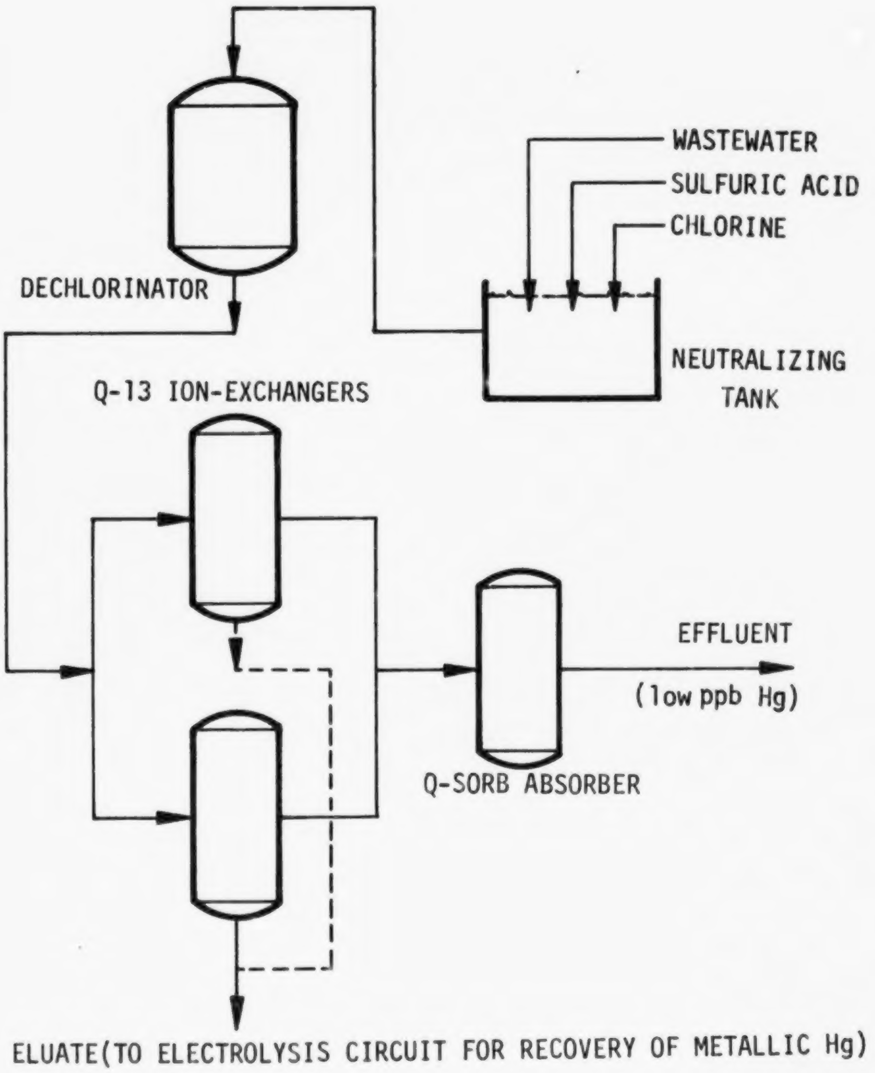

Figure 4. The Aktiebolaget Billingsfors-Langed Mercury Removal Process

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TABLE 1

MERCURY CONSUMED IN THE UNITED STATES BY USES

Use	Consumption, flasks				
	1964	1965	1966	1967	1968
Agriculture (includes fungicides and bactericides for industrial purposes)	3,144	3,116	2,374	3,732	3,430
Amalgamation	308	268	248	219	259
Catalysts	656	924	1,932	2,489	1,743
Dental preparations*	2,612	1,619	1,334	1,359	2,089
Electrical apparatus*	10,690	13,931	13,339	13,823	19,166
Electrolytic preparation of chlorine & caustic soda	9,572	8,753	11,541	14,306	17,424
General laboratory uses					
Commercial	1,583	1,119	1,563	1,133	1,202
Government	15,746	--	--	--	--
Industrial & control instruments*	4,972	4,628	4,097	3,865	2,841
Paint:					
Antifouling	547	255	140	152	8,611
Mildew proofing	4,898	7,534	7,762	6,151	
Paper & pulp manufacture	2,148	619	612	446	417
Pharmaceuticals	5,047	3,261	3,668	1,945	397
Redistilled*	11,697	12,131	7,267	7,334	8,418
Other+	7,734	15,402	15,632	12,563	7,805
	81,354	73,560	71,509	69,517	76,030

* A breakdown of the "redistilled" classification showed averages of 43 percent for instruments, 14 percent for dental preparations, 23 percent for electrical apparatus, and 20 percent for all other uses in 1963-1966, compared with 49 percent for instruments, 14 percent for dental preparations, 22 percent for electrical apparatus, 11 percent for general laboratory, and 4 percent for all other uses in 1967.

+ For 1964-1967, "other" includes mercury used for installation and expansion of chlorine caustic soda plants and vermillion.

TABLE 2

TRENDS IN USES OF MERCURY OVER THE PERIOD 1964 to 1968

Use	1968 Consumption Flasks	1968 Consumption Percent of Total
Increasing Level of Consumption		
Electrical Apparatus*	21,018	28.5
Electrolytic preparation of chlorine & soda	17,424	23.6
Paints	8,611	11.7
Catalysts	1,743	2.4
Subtotal	48,796	66.2
No Significant Changes in Consumption		
Agriculture	3,430	4.7
General Laboratory Use*	2,128	2.9
Redistilled	337	0.5
Amalgamation	259	0.3
Other uses	7,805	10.6
Subtotal	13,959	19.0
Decreasing Level of Consumption		
Industrial & Control Instruments	6,965	9.5
Pharmaceuticals	397	0.5
Dental Preparations*	3,120	4.2
Paper & Pulp Manufacture	417	0.6
Subtotal	10,899	14.8
Grand Total	73,654	100.0

* 1968 consumption in these categories was increased to include the quantity of redistilled mercury according to the 1967 percentile values given in Footnote* of Table 1.

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TABLE 3

ESTIMATED TRENDS IN CONSUMPTION OF MERCURY

Use	Estimated Mercury Consumption, flasks 1965	Estimated Mercury Consumption, flasks 1974-1975
Agriculture	3,430	2,650
Amalgams	259	250
Catalysts:		
Urethanes	300	1,560
Vinyl Chloride Monomer	500	250
Anthraquinone Derivatives	175	220
Miscellaneous	236	340
Dental Applications	3,500*	3,800*
Electrical Apparatus	17,200	22,700
Electrolytic Preparation of Chlorine & Soda	17,424	22,864
General Laboratory Use	2,075*	2,075*
Industrial & Control Instruments:		
Switches & Relays	2,500	2,650
Other Instruments	6,400*	6,600*
Paints	10,566	10,725
Paper & Pulp	375	250
Pharmaceuticals	600	650
Others+	7,815	5,960
Totals	73,855	83,544

* Includes some redistilled mercury.

+ Includes mercury requirements for start-up of new chlorine cells.

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TABLE 4

SOURCES OF MERCURY LOSSES FROM CHLOR-ALKALI PROCESS(0533, 2042, 2062, 2105)*

Source	Sweden (1967)	United States (1968)	Technically feasible (1970)
H_2 gas	27-85	180-230	0.01
NaoH	0.4-20	2-3	0.01-0.5
Brine sludge	2-50	5-125	0.1-1.0
Ventilation	15-25	5-45	0.5
Wash waters	10	5-70	0.01-0.1
Others	-	5-65	-
Total	55-190	202-538	0.63-2.11

* Grams of mercury lost per ton of chlorine produced.

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PROFILE REPORT

Nickel Ammonium Sulfate (290), Nickel Chloride (347), Nickel Nitrate (296), and Nickel Sulfate (298)

1. GENERAL

Introduction

Nickel ammonium sulfate [$NiSO_4 \cdot (NH_4)_2 SO_4 \cdot XH_2O$]; nickel chloride ($NiCl_2 \cdot XH_2O$); nickel nitrate [$Ni(NO_3)_2 \cdot XH_2O$]; and nickel sulfate ($NiSO_4 \cdot XH_2O$); are compounds of varying toxicity that find wide use in metal finishing, catalyst manufacture and battery manufacture, as well as minor uses in ceramics and general laboratory chemistry. Of the four compounds, nickel chloride and nickel sulfate are industrially important and their wastes are more widely spread. Nickel nitrate has limited uses while the ammonium sulfate is of little commercial significance. These four compounds represented 10 to 20 percent of the 273 million pounds of nickel consumed in the U.S. for all purposes in 1971. The bulk of nickel is used in ferrous, non-ferrous, and high temperature alloys.[0458]

Manufacture

The production methods for nickel ammonium sulfate, nickel chloride, nickel nitrate, and nickel sulfate can be generally characterized as reactions in which the appropriate acid is reacted with a source of pure nickel metal, nickel oxide, or nickel hydroxide. The desired nickel salt products are precipitated from the mother liquor which can be reused a number of times but finally must be dumped.[2160,2162]

The purification procedures are the focal point of the technology of providing pure salts and are believed to be the major source of nickel waste from their manufacture. Due to the proprietary nature of the critical purification steps, neither the details nor their waste outputs

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were available.[2160] However, the major manufacturers are recovering nickel values from their waste streams before final discharge. The majority of the production is on a batch scale and soda ash (anhydrous sodium carbonate) is added to the mother liquor. The precipitated nickel carbonate is washed and is used as starting material.[2162] The contacted manufacturers also had neutralization and clarification equipment at the plant for recovering nickel and other metal ions from the unsegregated waste streams flowing from all operations at the plant. The sludges from the in-plant treatment along with insoluble filter cakes and filter aids are landfilled.[2162,2163] The levels of nickel in plant effluents after final treatment were not available because of the reluctance of plant personnel to reveal them.[2160]

Electroplating and Metal Finishing

The electroplating industry is a significant contributor, if not the major source of water borne nickel wastes. Nickel sulfate and nickel chloride are the principal nickel salts used in the industry. Nickel ammonium sulfate has minor use to make "black nickel" surfaces. Water borne wastes in the metal finishing industry occur in six basic areas: (1) rinse water; (2) concentrated plating tanks accidentally or intentionally dumped; (3) washings from cleaning the plant equipment and facilities; (4) sludges, filter cakes, etc.; (5) regenerants or concentrates from in-plant water treating or recovery equipment; and (6) vent scrubber waters.

The predominant sources are the rinse waters, the concentrated plating baths, and sediments arising from purity maintenance on the tanks. The rinse waters are very dilute solutions containing nickel and other metals and anions, but because of their tremendous volumes, they represent the most serious pollution problem in the electroplating industry. The actual nickel plating baths can be maintained for long periods of time by means of procedures to remove impurities and maintain the effectiveness of the tank, but occasionally they are dumped and the effects of dumping such a large amount of plating solution at one time without treatment can have a disastrous effect on sewage lines, sewage treatment plants or aquatic life in open waterways. Typical effluents from metal finishing plants doing nickel plating are presented below:[0783]

TYPICAL NICKEL EFFLUENTS FROM PLATING SHOPS

Type of Work Plated	Volume gal/day	Ni Content ppm
Office machine	50,000	39
Silverware	40,000	33
Automobile manufacture	620,000	80
Metal fasteners	89,000	302

Only a very small percentage of plating shops are making any significant attempt to recover or treat waste nickel. The industry cites the lack of rigid discharge controls or limits of discharge set by municipal, state, and federal water pollution control authorities. Another reason for the prevailing discharge practices is that it is not economical to install recovery systems or plant wide water treatment systems in the average size plating shop. Only the high waste volume platers can benefit from recovering water and metal values.[2167] Furthermore sewer authorities more or less welcome certain metal ions in their sewer lines, nickel included, which react with and precipitate free sulfides within the sewer. This removes some of the corrosive and malodorous sulfides from the domestic sewage lines. The precipitated sulfides are recovered in primary clarification steps at the sewage treatment plant and thereby do not significantly effect the operation of the plant itself. More detail on the current situation within the metal finishing industry is presented in a large number of articles, reports and books. Notably among these, are Lund's book on industrial pollution control[0285], Metal Finishing Waste Disposal (article by Ceresa and Lancy)[1119] and a state-of-the-art review of metal finishing waste treatment with an extensive bibliography prepared by Batelle Memorial Institute.[0783]

Catalyst Preparation

Nickel nitrate and nickel sulfate are used as starting materials in the preparation of nickel catalysts for the petroleum and chemical industry. The big users buy these starting materials for captive production using proprietary processes. Examples are: (1) nickel sulfate chemically reduced to a catalyst powder; and (2) nickel nitrate solution saturated on a ceramic support and gently ignited to yield the desired impregnated nickel catalyst. These processes are believed to be on a batch basis with virtually no wasting of the starting materials.[2134]

Batteries

Nickel nitrate is combined with cadmium nitrate and saturated on inert fillers for "solid" electrolyte, nickel-cadmium batteries. The consumption of nickel nitrate in batteries is minor and significant wastes from the production of these batteries or their ultimate scrapping is not believed to occur.[0356]

2. TOXICOLOGY

Generally speaking the chloride, nitrate, sulfate and ammonium ions that are combined with nickel in the subject compounds assume the toxicological properties of the cation nickel. That is to say, if these compounds are inhaled or ingested, the toxicological effects of the nickel constituent would more likely cause a harmful effect before the ammonium, sulfate, nitrate, or chloride ions with which they are compounded.[0766]

Nickel compounds have been responsible for a variety of skin abnormalities among workers in refining plants, plating shops, and other industries where workers are in contact with them. Nickel salts have also been linked to carcinogenesis, especially when inhaled, but other materials were involved in these cases and the nickel compounds have not been proven as being singly responsible.[0615] The recommended threshold limit value for airborne nickel or nickel compounds is 1 milligram per cubic meter of air.[0225] Good discussions of the health and toxicological aspects of nickel and its compounds are found in a number of published works.[0356,0615,0633]

Studies have been made to investigate the toxic effects of nickel on plant life. In general, plants are more sensitive to nickel than lead. There also is a correlation between nickel and the iron content, copper content and pH of the soil which cause significant deleterious effects.[0633]

3. OTHER HAZARDS

The sulfate and nitrate anion constituents of the compounds being discussed in this Profile Report can release toxic fumes of SO_2 or NO_2 if they are exposed to intense heat. This represents a moderate disaster hazard if large amounts of these materials are involved in a very hot fire. The nitrate ion also is a source of oxygen and if combined with combustible materials, could represent a dangerous hazard from self-sustained combustion. In general, however, these compounds are considered to be stable and present no significant hazard when stored or transported under normal conditions.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Storage, Handling and Transportation

The subject nickel salts do not require severely restrictive storage, handling and transportation procedures. All four compounds are shipped in 100-lb plastic-lined paper bags. Nickel nitrate is also commonly shipped in 400-lb steel drums. Nickel chloride and nickel sulfate are also prepared in aqueous solution convenient for electroplaters. These solutions are shipped in 5-gal pails and 50-gal steel drums. It is recommended that personnel who handle open containers of these materials be provided with protective clothing, face shields and dust filtering breathing equipment to guard against possibility of skin contact and inhalation. Solid spills should be swept up and packaged for return to the manufacturer. Liquid spills require the addition of soda ash to precipitate nickel carbonate which can be sewered with additional large amounts of water.[0095]

Disposal

It is recommended that effluents discharged into open waterways contain not more than 0.05 ppm nickel compounds (calculated as nickel). The recommended maximum level of airborne nickel compounds, as nickel, is 0.01 milligrams per cubic meter of air. These limits of discharge can and are often exceeded when: (1) dilution quickly lowers the content to acceptable levels; and (2) discharges from other sources in the same region will not raise the nickel concentration in ambient air above dangerous levels. The anions of these nickel compounds can also effect the quality of water with regard to taste and laxative properties. The Public Health Service has recommended that waters containing more than 250 milligrams per liter (ppm) of chlorides or sulfates (or 500 milligrams per liter of total dissolved solids) not be used if other, less mineralized supplies are available. These levels are established primarily on considerations of taste. Laxative effects are not normally noted until sulfate concentrations approach 600 to 1,000 ppm. It is apparent that as long as the discharge limits for nickel are not exceeded, the discharge of the anions from nickel salts would not significantly add to any problem of water quality.

Reuse

Nickel prices are currently about $1.35/lb, a level where it is apparently economical only for manufacturers and large consumers to reclaim nickel values from waste solutions.[0285,1243,2162] The smaller plating and metal finishing shops normally do not have any water recovery or solution concentrating equipment. The only conservation procedure widely used is the "save rinse" method wherein rinse water in the first, most concentrated rinsing tank is added to the electroplating tank to make up for evaporative water losses.

5. EVALUATION OF PRESENT MANAGEMENT OPTIONS

Introduction

The nickel compounds being considered here are almost always found as wastes in aqueous solutions and two different approaches are typically employed in the management of these solutions. The first approach of waste management is reduction of these compounds in the final plant effluent or reduction of the volume of the stream itself. This is done by: (1) changing the processes to reduce waste outputs; (2) improving housekeeping; (3) segregating waste streams with specific recovery procedures; or (4) installing equipment for recovering water and concentrating the waste stream. The concentrated waste stream can then be more easily handled. The second approach is applied to the final plant effluent to remove the contaminants with no possibilities of reusing them. This usually means removal by precipitation of sludges. Firms trying to reduce and/or recover nickel wastes employ various techniques from both approaches when dealing with their wastes. Three good sources which provide overviews of the scope of the metal finishing waste problem and the state-of-the-art on treatment methods are presented in Lund's book, (an article by Ceresa and Lancy) and a report prepared by Battelle Memorial Institute.[0285,0783,1119]

Option No. 1 - Recycling and Reuse. The loss of large amounts of nickel compounds from the metal finishing industry, manufacturers and large consumers has created the need to adopt methods and equipment for recovering nickel values from these solutions. One of the easiest procedures for nickel conservation which is used in a great number of plating shops is that of "save rinse" which was described earlier. Other, more sophisticated equipment is commercially available to concentrate and recover nickel salt solutions for immediate reuse in the plant or to sell to an outside reclaiming firm. This equipment includes reverse osmosis, where the contaminated solutions are pressure-forced through a semi-permeable membrane. The permeate is recovered for rinse water and the concentrate is available for reuse or sale to a reclaimer. Multiple effect evaporators are used to concentrate solutions; thereby recovering the condensate for reuse or sale to a reclaimer as economics and purity of the concentrate dictate. The equipment also includes ion exchange which incorporates a bed of activated-beads through which the dilute aqueous solutions flow. Sites on these beads selectively attract and hold the desired ions. Periodically a regeneration solution is passed through the ion exchange beds and the adsorbed ions are desorbed from the bed in a concentrated solution. These concentrated solutions can be reprocessed for their metal values or otherwise recycled. Other newer methods are in various stages of development.

Option No. 2 - Precipitation and Clarification. Precipitation of insoluble nickel carbonate with soda ash (anhydrous sodium carbonate), or pH adjustment with caustic to yield the sludgelike, insoluble nickel hydroxide is a widely used method for treating aqueous nickel effluents. This process can produce treated effluents containing 1 to 5 ppm heavy metals when performed properly. The chemical companies manufacturing these nickel salts are actively recovering nickel from their large volume, batch, manufacturing processes for credit.[2160,2162] Whenever feasible plating shops also use soda ash to recover nickel values when a plating tank is completely rennovated. The $Ni(CO_3)_2$ can be redissolved in an appropriate mineral acid for immediate reuse, or may also be packaged, as is, for return to a reclaimer.[0285,1243,2162]

When caustic or an alkaline stream in the plant is combined with an acid plating shop effluent, the heavy metal hydroxides precipitate. These precipitates are normally gelatinous sludges with very high water content (70 to 80 percent). These sludges normally contain a wide mixture of materials and treatment after precipitation includes passage through a sand bed or similar clarifier. The sludge is removed for landfilling and the effluent is discharged to a municipal sewer or open waterway if permitted by the regulating authorities.

Option No. 3 - Direct Discharge to Municipal Sewers. Nearly all the small and medium size plating shops, and even some of the large ones, discharge their metal laden aqueous effluents to municipal sewers. Some plants have facilities to precipitate and clarify before discharge, as discussed above, but they are estimated to be about 15 percent of the total shops.[2134] In many areas, especially large metropolitan areas, this practice is allowed to continue as long as the toxicity of the nickel discharges has little or no effect on the continuous operation of any of the biological waste treatment processes of the sewage treatment plant. Many of the metal cations, nickel included, precipitate with sulfides in the domestic sewer lines while in transit to the sewage treatment plant. Thus, a great proportion of them are removed in the primary treatment process and most of the remainder are bound up in the sludge resulting from the secondary treatment processes.

The method is considered adequate provided that: (1) the sewage treatment authorities can effectively regulate the discharge of toxic metal compounds into the sewer system at a rate which will not disturb the efficiency of the sewage treatment processes; and (2) the operation and design of the sewage treatment plant is such that effective treatment is accomplished and the effluent from the treatment plant complies with the local purity regulations for discharge to open waters.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

National Disposal Site Facilities should not be made available to handle the subject nickel salts for the following reasons: (1) untreated wastes occur in dilute solutions that cannot be economically transported, (2) technology and waste handling techniques are available for those industries that choose to use them, and (3) wastes recovered from aqueous streams (precipitates) are being accepted by commercial dumps for landfill disposal. Landfilling these insoluble sludges or precipitates is adequate providing that the landfill has a proper geological location and that no materials, such as acids, are landfilled with the sludges which would cause them to redissolve and leach out. As a footnote, however, a National Disposal Site will be an excellent choice to process dried, metal laden sludges when the technology becomes available and the economics of processing are favorable. The potential for recovering metals from the tremendous volumes of these presently cumbersome and worthless materials would help in making the National Disposal system financially self sustaining.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nickel Ammonium Sulfate

IUC Name

Common Names double nickel salts
ammonium nickel sulfate

Structural Formula

$NiSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$

Molecular Wt. 395g/mole(2) Melting Pt. Boiling Pt.

Density (Condensed) 1.923g/cc(1) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 10.4g/100cc 20 C(1) Hot Water 30g/100cc 80 C(1) Ethanol insol

Others: Sol $(NH_4)_2SO_4$

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments used in electroplating

References (1) 1570
(2) 0766
(3)

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Nickel Nitrate hexahydrate

IUC Name

Common Names

Structural Formula

$Ni(NO_3)_2 \cdot 6H_2O$

Molecular Wt. 290.81g/mole(1) Melting Pt. 56.7 C(1) Boiling Pt. 136.7 C(1)

Density (Condensed) 2.05(1) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 238.5g/100cc @ 0 C(1) Hot Water very soluble(1) Ethanol soluble(1)

Others: NH_4OH

Acid, Base Properties aq soln:pH4

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments

References (1) 1570
(2) 0766
(3)

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Nickel Sulfate

IUC Name

Common Names

Structural Formula

$NiSO_4$*

Molecular Wt. 154.78g/mole(1) Melting Pt. d 848 C(1) Boiling Pt.

Density (Condensed) 3.68g/cc(1) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 29.3g/100cc @ 0 C(1) Hot Water 83.7g/100cc @ 100 C(1) Ethanol Insol

Others:

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments hexa and hepta hydrates lose water at 103 C and are more soluble in water and alcohol(1)

* Commercial products normally hydrated

References (1) 1570
(2) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nickel Chloride

IUC Name

Common Names

Structural Formula

$NiCl_2$*

Molecular Wt. 129.62 C(1) Melting Pt. 1001 C(1) Boiling Pt. Sub 973 C

Density (Condensed) 3.55g/cc(1) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ 1mm(2) @ 671(2) C

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 64.2g/100cc @ 20 C(1) Hot Water 87.6g/100cc @ 100 C(1) Ethanol Sol

Others: NH_4OH

Acid, Base Properties aq soln is acid pH4

Highly Reactive with

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments Not considered a systemic poison, can cause nickel itch in plating areas(2)

* Commercial products normally hydrated

References (1) 1570

(2) 0766

PROFILE REPORTS ON THE ANTIMONY, ARSENIC, AND SELENIUM COMPOUNDS OF NICKEL

Nickel Antimonide (291), Nickel Arsenide (292), and Nickel Selenide (297)

1. GENERAL

Nickel antimonide, nickel arsenide and nickel selenide are laboratory curiosities used in gram quantities for research and development. It is believed that the major research and development activities employing the arsenide and selenide is in semiconductors.[2135] The laboratory activities using the antimonide are not known. Sources at Rocky Mountain Research indicated that they are the sole manufacturers of these materials in the United States and they knew of no imports. They estimate that the national demand for these compounds is no more than 5 to 10 lb per year for each material. The actual details of manufacture for these compounds were not available, but it is believed that the method is either to: 1) roast the nickel in antimony, arsenic or selenium vapor, or; 2) combine the elements in a sintering process.[2133] Their very small production and value would indicate, that in all likelihood, no significant amounts of the material are being lost to the environment as waste products. In addition, no evidence of any of these compounds being produced as a waste product from other unrelated processes was found.

Nickel arsenide, even though it is commercially produced in high purity, also occurs naturally as niccolite, the least of the three principal nickel ores; the others being the nickel sulfides and nickel oxides. Niccolite is said to have no current commercial importance as a nickel bearing ore.[0300] Niccolite ores are not processed in the United States and any study on NiAs wastes from foreign processing is outside the scope of this study.

2. TOXICOLOGY

The antimony, arsenic, and selenium constituents of the subject materials are the principle source behind the hazardous nature of these

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compounds. Most arsenic compounds are poisons whereby the systemic effects are normally caused by ingestion. As little as 0.1 grams can be fatal if taken internally. Both nickel and arsenic can be responsible for a variety of skin abnormalities on contact. Acute poisoning symptoms from ingesting arsenic compounds may include difficulty in swallowing, severe abdominal pain resulting from corrosion of the stomach lining, vomiting, with pain in the limbs and muscle cramps. A cold damp skin, a rapid and weak pulse, shock, unconsciousness and convulsions are the indicators of impending death. The symptoms caused by chronic low level arsenic exposure are difficult to diagnose due to the wide variety of unpredictable symptoms which may arise.[0766]

Selenium compounds with nickel are considered as moderate toxicological hazards that when taken orally can cause both irreversible and reversible changes that are not severe enough to cause death or permanent injury.[0766] Selenium compounds have low systemic toxicity but in dust form, they can be dangerous respiratory tract irritants as are most nickel compounds. All three compounds, when inhaled, can cause death or permanent injury even after very short exposure to small quantities.[0356] The recommended threshold limit value of 0.2 milligrams per cubic meter of air represents the maximum concentration to which personnel should be exposed in an 8-hour period. Nickel has been identified with respiratory carcinogenesis, but that is subject to debate since the cited cases involved other materials with nickel compounds.[0633]

Antimony compounds are also highly toxic when ingested or inhaled. Small amounts can cause permanent injury or death. The recommended TLV is 0.5 mg per cubic meter of air.[0766] Information on the toxicity of these compounds towards other animals and plant life was not found.

3. OTHER HAZARDS

Nickel arsenide and nickel selenide both exhibit moderate to serious fire, explosion, and disaster hazards as a result of being heated or exposed to water, steam or acids. These reactions will emit the highly flammable arsines and hydrogen selenides which, if present in the right proportions with air, could explode if ignited. Stibine (H_2Sb), arsine (H_3As), and hydrogen selenide (H_2Se) vapors are all extremely toxic and represent a serious disaster hazard if released in areas where they might be inhaled by humans or animals.[0766] Nickel antimonide and the potentially evolved hydrides of all compounds react violently with oxidizing agents.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage and Transportation

The toxicological and flammable hazards of these materials require careful handling when they occur as waste products in a concentrated form. They should be stored in containers in which they are compatible, i.e. screwtop glass bottles or ampules. They should be stored in cool areas with no prevalent acid mists. The use of protective clothing, eyewear and dust filtering respiratory equipment are recommended for handling these materials outside fume hoods. Spills of the solid materials should be cleaned up using a vacuum cleaner with a disposal paper dust bag. No DOT or ICC regulations are prescribed by Sax, but common sense recommends careful labeling on both the bottle and shipping container.[0766]

Disposal/Reuse

The disposal of the antimonides, arsenides and selenides of nickel into the air, water, or soil is completely unacceptable from the standpoint of the toxic nature or antimony, arsenic, selenium, and the somewhat less toxic but still significant hazard of nickel. The U.S. Public Health Service has established 0.05 mg/l arsenic content as grounds for rejecting a drinking water supply. The ideal maximum is 0.01 mg/l.[1752] The Public Health Service in its publication on drinking water standards recommended that the limits for selenium be lowered from the present value of 0.05 mg/l to 0.01 mg/l and concentrations in excess of this lower value be used as grounds for rejection of the water supply.[1752] It is recommended that the amounts of airborne nickel arsenide and nickel selenide not exceed 0.01 milligrams per cubic meter of air for continuous exposure.

All three compounds are expensive (estimated prices for ten grams each of the antimonide, arsenide, and selenide being $40, $33 and $9 respectively), and in light of this, it would appear that reasonable attempts would be made to prevent indiscriminate wasting of the compound. Small amounts of these materials, if occurring as wastes in a concentrated form, should be packaged and returned to the supplier or manufacturer for reprocessing, purification, or ultimate disposal. Considering the low levels of use for these compounds (5 lb per year), it is not expected that these materials would occur as wastes in any significant amounts. Shipping waste concentrates back to the manufacturer is the cheapest and safest way of handling them. Rocky Mountain Research, currently the only apparent manufacturer of these materials, expressed its willingness to accept returned waste concentrates.

5. EVALUATION OF CURRENT DISPOSAL METHODS

Option No. 1 - Return to Vendor or Manufacturer. The amounts of concentrated waste nickel antimonide, arsenide, or selenide which could arise are expected to be very small. For this reason, careful packaging and shipment back to the vendor or manufacturer by prior arrangement is an easy and safe means of disposal. The manufacturer can either reprocess the material, if economically feasible, or could dispose of it in his own facilities. Return to the manufacturer or vendor should be considered before any other disposal option is considered.

Option No. 2 - Encapsulation and Landfill. Some landfills are chartered to accept these compounds for ultimate encapsulation and landfill. They would most likely be combined with other compliant materials in a steel drum, and the steel drum would be given a concrete collar before burial. No cost estimates for such an operation were determined, but it is felt to be costlier than mailing or otherwise shipping these compounds back to the manufacturer as stated in Option No. 1. Landfilling is, however, still feasible and currently adequate.

Option No. 3 - Laboratory Decomposition to Reduce Hazard. The subject materials can be roasted in air or oxygen to produce the condensable poisonous oxides of antimony, arsenic, and selenium and non-volatile nickel oxide. The fire hazards are lower with these products, but there remains the problem of disposing the toxic products. This option is felt to be unwarranted when the costs are compared to the benefits.

6. APPLICABILITY OF NATIONAL DISPOSAL SITES

No recommendation is made for any equipment or waste treating processes to treat waste nickel antimonide, nickel arsenide, or nickel selenide at a National Disposal Site. It is estimated that the annual production of these materials, as wastes, does not exceed 10 pounds. Furthermore, they are rather expensive compounds and it is doubtful that they would be wasted.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nickel antimonide

IUC Name

Common Names Breithauptite(1)

Structural Formula

$NiSb$(1)

Molecular Wt. 180.6(1) Melting Pt. 1158 C(1) Boiling Pt. d1400 C(1)

Density (Condensed) 7.54(1) @ Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water Hot Water reacts Ethanol

Others:

Acid, Base Properties

Highly Reactive with steam to form stibine(2). Can also react violently with oxidizing agents.(2)

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments slight explosive hazard when exposed to flame, can evolve stibine(2); releases antimony vapors when heated to decomp temp.

References (1) 1570
(2) 0766

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Nickel Arsenide

IUC Name

Common Names Niccolite(2)

Structural Formula

NiAs

Molecular Wt. 133.60(2) Melting Pt. 968 C(2) Boiling Pt.

Density (Condensed) 7.57 g/cc @ 0 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble Hot Water reacts with steam Ethanol

Others: acids (reaction)

Acid, Base Properties

Highly Reactive with hot water, steam and acids to produce toxic and flammable vapors of arsenic hydrides(2)

Compatible with

Shipped in glass bottles

ICC Classification Coast Guard Classification

Comments Highly toxic, moderate chem. reaction to form arsine, a fire and explosion hazard.

References (1) 1570
(2) 0766

HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name Nickel Selenide

IUC Name ____

Common Names ____

Structural Formula

NiSe

Molecular Wt. 137.67(1) Melting Pt. Red heat(1) Boiling Pt. ____

Density (Condensed) 8.46 @ ____ ____ Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____ ____ @ ____ ____ @ ____

Flash Point ____ Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water insoluble Hot Water reacts Ethanol ____

Others: soluble in acids; reaction

Acid, Base Properties ____

Highly Reactive with water steam and acids to produce toxic and flammable vapors of hydrogen selenide

Compatible with glass

Shipped in glass bottles

ICC Classification ____ Coast Guard Classification ____

Comments Fire hazard: evolves hydrogen selenide, a toxic gas.

References (1) 1570
(2) 0766

PROFILE REPORT

Perchloryl Fluoride (326)

1. GENERAL

Perchloryl fluoride, ClO_3F, is the acyl fluoride of perchloric acid. It is a remarkably stable compound of low reactivity that is shipped as a compressed gas. Perchloryl fluoride gas is colorless and the liquid is clear and water-white. It has a characteristic sweet odor. The oxidizing potential of perchloryl fluoride is high and becomes available in the combustion of fuels which has resulted in its evaluation as a storable liquid oxidizer for rockets. In an alkaline environment, perchloryl fluoride selectively replaces labile hydrogen with fluorine; this property is in use in the preparation of certain fluoro-steroids. In the presence of Friedel-Crafts catalysts, perchloryl fluoride can introduce the ClO_3 group onto aromatic rings giving a new class of perchloryl aromatic compounds.

Perchloryl fluoride is prepared by the electrolysis of sodium perchlorate dissolved in anhydrous hydrogen fluoride. The stability of perchloryl fluoride is due to its molecular symmetry. On the other hand, the reactivity of its component elements can be released at a controlled rate. Anhydrous perchloryl fluoride is thermally stable up to 500 C. The chemical reactivity is primarily dependent on pH, temperature and the presence of the other reactive atoms or molecules in the reaction media. It is resistant to hydrolysis; water at 250 to 300 C has very little effect on perchloryl fluoride. In sealed tubes at 250 to 300 C it reacts with alkali metal hydroxides to give a quantitative hydrolysis to perchlorate and fluoride ions. Alcoholic potassium hydroxide causes rapid hydrolysis of perchloryl fluoride at 25 C.[2152]

The physical/chemical properties for perchloryl fluoride are given in the attached work sheet.

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2. TOXICOLOGY

Should liquid perchloryl fluoride splash on the skin, moderate to severe frostbite "burns" may occur depending on the amount spilled and the length of time on the skin. However, toxic injury to the skin is unlikely.

Moderate to high concentration of the vapor causes respiratory irritation and methemoglobinemia. If severe, methemoglobinemia is accompanied by cyanosis. Repeated long term exposure to low concentrations of perchloryl fluoride may cause fluorosis of fluoride deposition in bones and teeth. This conclusion is based on the detection of significant increases of fluoride concentrations in the blood, urine and bones of rats, dogs, and guinea pigs exposed to 25 ppm concentrations for six months.[2153]

The threshold limit for an 8-hour day, 5 days per week is 13.5 mg/m^3 (3 ppm) (ACGIH).[0225] The maximum emergency exposure limits are as follows:[1300]

10 minutes	170 mg/m^3	(50 ppm)
30 minutes	68 mg/m^3	(20 ppm)
60 minutes	34 mg/m^3	(10 ppm)

3. OTHER HAZARDS

A system containing liquified perchloryl fluoride in the presence of an oxidizable substance may be shock sensitive, in a fashion similar to that encountered with liquid oxygen. Therefore, caution must be exercised to prevent contamination of perchloryl fluoride from occurring. No attempt should be made to absorb, condense, or liquify effluent gases from reactions.[1300,2154]

Many perchloryl derivatives, both organic and inorganic, demonstrate shock sensitivity. Sufficient heat or mechanical impact may cause detonation.[2154]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Anhydrous perchloryl fluoride does not attack glass, corrode metals, or attack common gasketing materials rapidly at ordinary temperatures. It can be stored for extended periods, as shipped, ready for immediate use. Anhydrous perchloryl fluoride has been stored at 70 F in steel cylinders for periods of several years without evidence of instability. Shorter term storage tests at 100 F have given equally favorable results.[2153]

The maximum temperature recommended for prolonged storage in metal containers is 130 F. Perchloryl fluoride in gaseous and liquid states is stable to shock.[2154]

In the presence of water vapor, perchloryl fluoride becomes corrosive to many metals. Stainless steels, types 304, 310 and 314 have shown favorable short-term exposure tests at 25 C for two-month exposure. Other metals exhibiting good resistance under these conditions include Hastelloy, titanium and tantalum.[2154]

Perchloryl fluoride is shipped by rail, truck, or vessel. Air freight, parcel post, and rail express are permitted; it is not approved for air express shipment. The loaded pressure in cylinders at 70 F is 145 psig. Perchloryl fluoride is classified by DOT as a "Compesssed Gas, Not Otherwise Specified." A green DOT label is required during shipment.[2153]

Recommended maximum concentrations of perchloryl fluoride for release to the environment from waste disposal processes are as follows:

Containment and Environment	Maximum Recommended Concentration	Basis for Recommendation
Perchloryl fluoride released to the atmosphere within the boundaries of a plant	13.5 mg/m^3 per 8 hours exposure	TLV
Perchloryl fluoride released to the atmosphere outside the boundaries of a plant	0.15 mg/m^3	0.01 TLV

5. EVALUATION OF CURRENT AND NEAR FUTURE PERCHLORYL FLUORIDE DISPOSAL PROCESSES

The processing options for the disposal of perchloryl fluoride are briefly described in the following paragraphs together with recommendations as to their adequacy. Detailed discussions of the processing operations are presented in the referenced perchloryl fluoride reports.

Option No. 1 - Reaction with a Charcoal Bed

The classic fluorine disposal unit is a charcoal bed composed of 3/8-in. charcoal bits.[1154] This method has been used with fluorine, with interhalogen compounds (ClF_3 and ClF_5) and with perchloryl fluoride.[1300] The products are carbon tetrafluoride, carbon dioxide, and chlorine. Carbon tetrafluoride is chemically inert and relatively non-toxic which permits it to be vented.[1414] Chlorine and carbon dioxide produced are removed by a caustic scrubber. Perchloryl fluoride is highly hypergolic with either amorphous carbon or charcoal and reacts vigorously under all conditions, even at low concentrations.[2154] If high rates of disposal are required for perchloryl fluoride, the charcoal reactor will become a huge furnace. However, for fluorine, the charcoal disposal system has proven successful for disposal rates up to 600 lb per hr (30 lb of fluorine in approximately 3 min). Continuous operation requires a number of parallel disposal reactors. Approximately 17 lb of charcoal are required to treat 100 lb of fluorine.[1154,1414] On this basis, about 22 lb of charcoal would be required per 100 lb of ClO_3F. Engineering data for perchloryl fluoride similar to that obtained for fluorine has not been obtained, but is required to adequately design a charcoal reactor for perchloryl fluoride.

Option No. 2 - Propane Burner

A propane burner has been described for the disposal of oxygen difluoride which could be used for perchloryl fluoride.[1414] The unit consists of a burner, stack, propane supply and control system and an air blower. The fluorine compound is discharged into the burner, which is run rich in propane. Both hydrogen fluoride and chloride are exhausted and require scrubbing. Such a unit, though not in use, should be satisfactory for treating large quantities of perchloryl fluoride.

Option No. 3 - Venting

One propellant handling manual recommends disposal of perchloryl fluoride in an isolated, posted area by remotely controlled dumping through a pipe to a shallow evaporating pan where the material is allowed to evaporate.[1300] This method is not considered satisfactory because the vapors discharged are reactive and toxic.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

It is recommended that National Disposal Sites have a unit operation capable of handling perchloryl fluoride, fluorine, interhalogen compounds and chlorine. Since this unit operation will not be required to handle large volumes of these compounds, the unit can contain options for treating each of these compounds. It is recommended that experimentation be conducted to generate the necessary engineering data for construction of such a unit. Option 1, Reaction with a Charcoal Bed, is recommended for use at a National Disposal Site because this method has been adequately evaluated for treatment of fluorine and has been used in the laboratory for treatment of perchloryl fluoride.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Perchloryl fluoride

IUC Name Perchloryl fluoride

Common Names

Structural Formula

ClO_3F

Molecular Wt. 102.45 Melting Pt. -147.7 C Boiling Pt. -46.67 C

Density (Condensed) 2.003 @ 147.7 C Density (gas) 0.065 g/cm^2 @ 25 C

Vapor Pressure (recommended 55 C and 20 C)

2.25 psia @ -80 C 84.01 psia @ 0 C 176.0 psia @ 25 C

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 0.1 g/l at 25 C Hot Water Ethanol 2.5 g/l at 25 C

Others: dioxane 5.0 g/l at 25 C

Acid, Base Properties acts as a Lewis base in Friedel-Crafts type reactions

Highly Reactive with H_2S, N_2H_4, nucleophilic groups, carbon

Compatible with most metals, water

Shipped in steel cylinders

ICC Classification compressed gas, nos Coast Guard Classification compressed gas nos

Comments critical temperature 95.9 C
critical pressure 779 psia

References (1) 2154

PROFILE REPORT

Sodium Chlorate (385)

1. GENERAL

Introduction

Sodium chlorate, $NaClO_3$, is a white crystalline solid which is slightly hygroscopic. The compound is a soluble oxidizing agent in acid and neutral solutions, but in basic solutions at room temperature it does not show oxidizing properties.

In acid solutions, sodium chlorate is a source of chloric acid, a powerful oxidizing agent. Chlorates are strong oxidizers, comparable to manganese materials and chlorine. They are stronger than bromates or iodates. The molten salt is also a powerful oxidizing agent.[2122]

In 1969, there were 187,125 tons of sodium chlorate produced in the United States. In 1970, the production was 221,000 tons and the projected annual demand for sodium chlorate by 1974 is 265,000 tons.[1596]

Manufacture

All of the chlorate produced in the United States is prepared by electrolysis of a solution of chloride and chlorate in a diaphragmless cell.[1433]

A number of reactions take place at the anode. Chlorine is liberated and reacts with hydroxide ion to produce hypochlorite and chloride ions: and with water to form hypochlorous and hypdrochloric acid:

$$2\ Cl^- \longrightarrow Cl_2 + 2e$$

$$Cl_2 + 2OH^- \longrightarrow ClO^- + Cl^- + H_2O$$

$$Cl_2 + H_2O \longrightarrow HClO + H^+\ Cl^-$$

By maintaining the electrolyte at pH 6.2 to 7, favorable conditions for the reaction between hypochlorous acid and hypochlorite ions can be maintained, so that chlorate is formed. This is a slow reaction, and takes place in the body of the cell rather than at or near the anodes.

The reactions for the electrolyses of sodium chloride, and for the formation of hypochlorus acid and hypochlorite ion from the evolved chlorine, may be combined with the reaction for the hypochlorous acid-hypochlorite ion to form chlorate, giving the overall reaction:

$$NaCl + 3H_2O \longrightarrow NaClO_3 + 3H_2$$

Six faradays are required per mole of sodium chlorate formed; the overall reaction is 100 percent efficient.[1433]

Large scale commercial facilities for the manufacture of sodium chlorate include the following[1506]:

Kerr-McGee Chemical Corporation; Hamilton, Mississippi and Henderson, Nevada

Hooker Chemical Corporation; Columbus, Mississippi

Penn-Olin Chemicals; Calvert City, Kentucky.

Uses

Sodium chlorate is used extensively as a source of chlorine dioxide for paper pulp bleaching. It is used in tanning and finishing leather, in processing of furs, in the preparation of dyes, as a mordant in textile dyeing and printing, for production of bromine from brines, for medicinal purposes, in metaullurgy operations, processing of uranium ore, and as an intermediate in the production of perchlorates. In agriculture, it is used as a cotton and tomato defoliant, and it is used as a weed killer. Battery-active manganese dioxide can be made by a chemical process using sodium chlorate oxidation of manganese. It is also a selective oxidizing agent in organic synthesis.[2122]

Sources and Types of Sodium Chlorate Wastes

The sources of sodium chlorate wastes may include the following: 1) sodium chlorate manufacturers; 2) sodium chlorate wholesalers; 3) agricultural users; 4) government facilities that store, transport, and use sodium chlorate; 5) commercial and industrial processes including those from paper manufacturers, textile dyeing and printing operations, metallurgy operations, etc.

In general, most of the sodium chlorate waste will be in concentrated form as a result of spills occuring in the transporting and handling of the materials. The electrolytic process used in manufacturing sodium chlorate is a closed process and no waste is generated other than accidental spills or the small amount of chlorate, mixed with other solids which is left as residue after the filtering process. In the bleaching process (in paper manufacturing) there is essentially a 100 percent conversion of sodium chlorate to chlorine dioxide, so there is no waste chlorate, other than spills involved in handling the material.[2120]

Dilute sodium chlorate wastes include those generated in agricultural runoffs and possible spent solutions used to clean empty containers.

Physical and Chemical Properties

The physical and chemical properties of sodium chlorate are included in the attached worksheet.

2. TOXICOLOGY

Sodium chlorate is not highly toxic, but ingestion or excessive inhalation of dust should be avoided. Ingestion of relatively large quantities (15-30 gm) of the material may prove fatal. Abdominal pain, nausea and vomiting, diarrhea, pallor, blueness, shortness of breath, unconsciousness and collapse are the immediate symptoms following ingestion of toxic amounts of sodium chlorate. Prolonged exposure to sodium chlorate dust may cause skin irritation to the mucous membranes of the eyes, nose and throat.[2123]

The intraperitoneal LD_{50} value of sodium chlorate to the mouse is 550 mg/kg of body weight.[1312]

3. OTHER HAZARDS

Sodium chlorate is a strong oxidizing agent and constitutes an extreme fire and explosion hazard if allowed to come in contact with organic or combustible materials, acids, or reducing substances.

Dry materials such as wood, clothing, paper, and leather contaminated with sodium chlorate may easily be ignited by friction, percussion, or any source of heat such as flames, sparks, welding torches, lighted cigarettes, and hot surfaces. Ignition can also occur when sodium chlorate dust comes in contact with clothing that is damp with perspiration and which then dries.[2124]

Mixtures of sodium chlorate with oxidizable organic substances such as oils, greases, waxes, solvents, paints, sugars, alcohols, wood dust, lint, and vegetable dusts are potential fire and explosion hazards.

Certain easily oxidizable or finely divided inorganic materials such as ammonium compounds, sulfur and its compounds, sulfides, phosphorous, powdered metals, and metal salts (especially copper) are potential fire and explosion hazards when mixed with sodium chlorate.[2124]

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transporation

In handling chlorates, workers should wear clean coveralls daily, as well as washable rubberized gloves, boots or shoes. A washable head covering should also be used. In dusty conditions, goggles and an approved dust respirator should be used. Use of leather shoes or gloves is not recommended because when contaminated it may not be possible to remove completely all traces of chlorate from the leather. Workers should avoid using oils, greases or protective creams on skin, as flammable mixtures may develop on prolonged contact of these materials with chlorates.[2123]

Dry bulk sodium chlorate should be stored in lined steel, concrete or tight glazed tile silos or tanks. Dessicated air should be supplied to prevent caking from atmospheric moisture. Storage of sodium chlorate in drums should be in a cool, dry, fireproof building. Dry concrete floors are preferable to wooden decks. Spillage should be swept up and removed at once. Sodium chlorate solutions or slurries may be stored in steel-lined tanks.[2123]

Sodium chlorate is shipped in metal drums (returnable and single trip) and in tank cars. It is classified by the Interstate Commerce Commission (ICC) as an oxidizing material and must be packed in ICC specification containers when shipped by rail, water or highway. All of the ICC regulations regarding loading, handling, and labeling must be followed.[2123]

Disposal/Reuse

Contaminated or degraded sodium chlorate cannot be practically considered for reprocessing. Contaminated sodium chlorate must be disposed of by one of the methods described in Section 5.

Although sodium chlorate is very soluble in water, it does not appear to be a serious water pollution problem. The small amount of sodium chlorate that is discharged into sewers, lakes, or streams will readily supply oxygen to the BOD or COD present in the water and be reduced to the chloride ion. Also, chlorate ion will be rapidly reduced to the chloride ion by any other reducing agent present in the water.[2120]

5. EVALUATION OF CURRENT AND FUTURE DISPOSAL SITES

Option No. 1 - Reduction. The most acceptable method for disposing of both solid and aqueous sodium chlorate waste is to reduce it with a reducing agent in a plastic vessel. If the waste is present in the solid form, it is first dissolved and then reduced in the vessel. The most economical and readily available reducing agent is iron filings. Pickle liquor from the iron and steel industry is also a good reducing agent. The sodium chlorate is reduced to sodium chloride in the reduction process and the resulting iron precipitate can be removed with a lime slurry, soda ash, or sodium hydroxide followed by a lagooning operation.[2121]

Option No. 2 - Incineration. A small amount of sodium chlorate waste can be incinerated if it is mixed with a large quantity of other combustible waste. An adequate gas clean up to remove the gaseous combustion products must be installed to alleviate the air pollution problem.[2121]

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Considering the small amount of waste sodium chlorate present in industry and the lack of a severe water pollution problem associated with the compound, it is felt that sodium chlorate does not warrant National Disposal Site treatment. The simple method of disposing of sodium chlorate by reduction with ferrous ion can easily be performed by a firm that handles the compound. In summary, processes for the exclusive treatment of sodium chlorate are not recommended for inclusion in the National Disposal Site scheme.

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#385

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Sodium Chlorate

IUC Name

Common Names Sodium Chlorate

Structural Formula

$NaClO_3$

Molecular Wt. 106.45 Melting Pt. 248 C Boiling Pt. Decomposes @ 300C

Density (Condensed) 2.490 @ 15 C Density (gas) @

Vapor Pressure (recommended 55 C and 20 C)

@ @ @

Flash Point Autoignition Temp.

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water 79 g/100 g @ 0C Hot Water 140g/100 g @50 C Ethanol

Others:

Acid, Base Properties

Highly Reactive with organic substances, solvents, oils, sulfur sulfides, phosphorous, powdered metals and ammonium salts.

Compatible with Sulfates, carbonates, nitrates and oxides.

Shipped in metal drums (returnable and single trip), tank cars.

ICC Classification oxidizing material, yellow label Coast Guard Classification oxidizing material, yellow label

Comments

References (1) 0766.

PROFILE REPORTS ON
THE TRIVALENT CHROMIUM SALTS

Chromic Fluoride (485), Chromic Sulfate (486), Chromium Cyanide (487)

1. GENERAL

The salts of trivalent chromium, Cr III, are moderately poisonous materials. Of the three compounds in this profile report, only two have any commercial significance. They are chromic fluoride, CrF_3, and chromic sulfate, $Cr_2(SO_4)_3$. Chromium cyanide is not believed to exist at all; a fact to be detailed later. Chromic fluoride was found to have some uses in the textile industry as part of the dyeing operation. Chromic sulfate is extensively used in the leather tanning and finishing industry in a modified, basic form.

Chromic Sulfate

Normal chromic sulfate, $Cr_2(SO_4)_3$ is of no commercial importance, but the so-called basic chromic sulfates are produced in large amounts for use in the leather tanning industry, and are incorporated in various proprietary chrome tan mixtures. These basic chromic sulfate tanning solutions can either be made commercially and supplied to the tanning industry or be prepared directly in the tanning vats. The normal preparation process is the reduction of a sodium dichromate solution with either an organic material (Equation No. 1) or sulfur dioxide (Equation No. 2).[2055] The organic reduction using crude molassis, corn sugar, and sometimes even sawdust is the older and more widely used method. Sulfur dioxide, when used, plays the dual role of reducing agent and, upon oxidation, of furnishing the required sulfate. If sugar is used, sulfuric acid must be added.

$$8Na_2Cr_2O_7 + 24H_2SO_4 + C_{12}H_{22}O_{11} \rightarrow 16Cr(OH)SO_4 + 8Na_2SO_4 + 27H_2O + 12CO_2 \quad (1)$$

$$Na_2Cr_2O_7 + 3SO_2 + H_2O \rightarrow 2Cr(OH)SO_4 + Na_2SO_4 \quad (2)$$

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The actual composition of the product is much more complicated than that indicated by the formulas shown. The chromic sulfate produced by these reactions is described as one-third basic since, stoichiometrically, only two-thirds as much sulfate is combined with the chromium as in the normal sulfate. A whole range of basicities is available to the tanning industry for different types of tanning. The production of basic chromic sulfate is performed on a batch basis, and if prepared at the tannery, the hides are added to the same vat in which the reduction took place. No purification of the commercial product is performed before it is spray dried and packed. It is believed that the manufacture of basic chrome sulfate results in no significant amounts of contaminated waste solids or liquids.

The actual chrome tanning of the hides however does create very large amounts of chromic sulfate wastes in aqueous solution resulting from the tanning and subsequent washing of the hides. Hide tanning, by definition, essentially consists of removing organic matter from the hides,thus preserving them. This organic matter, if allowed to build up in the chrome tanning solutions would interfere with the tanning process. Therefore the solutions are normally dumped after being used once or possibly twice. There are incomplete details on some tanneries that are renewing their chrome tan solutions with more concentrated chromic sulfate rather than dumping the spent tan solutions They claim that some chromium tan solutions are being reused as many as 15 times without detrimental effects. This situation is currently the exception and not the rule.[0087]

An additional, proposed chrome sulfate conservation technique is to precipitate chromium hydroxide from the chrome tanning solutions, filter it,and then redissolve it with sulfuric acid. This technique can remove some of the organic water and allow reuse but most tanners consider the process to be economically impractical and the greater proportion of the tanneries are only using their tanning solutions once.

The majority of tanneries are located in or near large metropolitan areas to permit the utilization of municipal or joint water treatment facilities.[0087] The cities are always the meat packing centers, i.e., Chicago, Milwaukee or Los Angeles. It is estimated that 80 percent of the tanning wastes are being discharged to sewers for treatment by municipal waste water treatment plants. The remaining 20 percent are being treated in onsite plants for solids and BOD reduction before discharge to sewers or waterways. The quantity of trivalent chromium in inadequately treated tannery effluents discharged to open waterways, if any, was not determined because of the obvious difficulties in obtaining such sensitive information, but it is expected that future further tightening of discharge limits will result in no discharges from tanneries into open waterways.

Chromic Fluoride

Chromic fluoride is used in the textile industry as a dyeing aid and mordant. Other trivalent chrome compounds can be used in its place. The constantly changing processes in the textile industry as well as the free substitution of different chemicals for process applications makes it difficult to determine exactly how much chromic fluoride is being used, but it is believed that its consumption is very small.[2053,2054,2055]

The completely anhydrous chromic fluoride is insoluble and is not used in the textile trade. Two hydrated compounds are commercially available. They are $CrF_3 \cdot 4H_2O$ and the more soluble $CrF_3 \cdot 9H_2O$. These compounds and their basic, complex compounds are used as mordants for wool, in aftertreating oxidation sensitive direct cotton dyes, and with special mordant acid dyes in the printing of worsted woolen. It has also been stated that chromic fluoride imparts some moth-proofing qualities.[2055]

When used, chromic fluoride is contained in vats and is exhaustively deposited on the textile that is either dipped or run through continuously. A significant portion of solution is lost by transfer to subsequent rinsing and post treatment tanks.

The wastes from textile mills are characteristically mixtures of the effluents from many different processes since most mills do not segregate waste streams. Most of the Southern mills have some sort of on-site water treatment facilities whereby chromium and other heavy metal wastes are removed by precipitation through pH adjustment techniques. An official of the American Association of Textile Chemists and Colorists indicated that virtually all of the Southern mills have responded to the needs for some water treatment. They either operate their own on-site water treatment facilities or are cooperating with a neighboring city for joint municipal treatment. The Northern textile mills, benefiting from the greater availability of water, are characterized as normally sewering their trivalent chromium wastes and diluting it as required for municipal treatment.[1480]

Chromium Cyanide

No references to chromium cyanide could be found in the literature, after an exhaustive search, except for a brief discussion of chrome cyanide compounds by Udy.[2055] Chromous cyanide and chromic cyanide are products of reactions under exacting conditions between KCN and $CrCl_2$ or $CrCl_3$ respectively. They decompose quickly in air and often undergo a variety of additional reactions in solution. No uses were identified by Udy or in any of the literature investigated in preparing for this profile report. A maker or supplier of chromium cyanides could not be found and no process or industry could be identified which might produce chromium cyanides as a waste from any process. The presence of chromic cyanide was described by one source as a highly unlikely occurrence since cyanides can only exist in an alkaline media which would ordinarily precipitate trivalent chromium.[1981] No physical properties were found in any of the standard works that are consulted in these studies and identified in other profile reports.

2. TOXICOLOGY

Trivalent chromium compounds are said to be slightly less toxic than the hexavalent chromium compounds. Eczema-like skin conditions from trivalent chromium contact have been reported.[0766] The toxicology literature discusses the hexavalent compounds in considerable detail but the available literature does not distinctly describe the hazardous properties of the trivalent compounds by themselves. The Threshold Limit

Value for trivalent chrome compounds is 0.5 mg per cubic meter.[0225] Internally, chrome salts act as an irritant causing tissue corrosion in the gastrointestinal tract. Complaints of a bad taste in the mouth, vomiting and bloody stools are often noted. In addition, the central nervous system is often involved and dilated pupils, coma, collapse, slow respirations, shock and death sometimes occur.[2028]

When drinking water contains fluoride in relatively low concentrations, it will help prevent dental caries. No ill effects will result from these small amounts of fluoride. Excessive fluoride which is ingested by drinking water with high fluoride content or ingesting other fluoride contaminated materials will produce an objectionable dental fluorosis accompanied by an embrittlement of bones. The fluorosis in bones can have a crippling effect when 20 or more milligrams of fluoride from all sources is consumed per day for 20 or more years. Death will occur when 2.2 to 4.5 grams of fluoride is consumed in a single dose.[1752]

Other Hazards

No other flammability or explosive hazards have been found to exist for these compounds.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

The toxicity of the trivalent chrome compounds necessitates the use of careful precautions when storing, handling, transporting, disposing or reusing these materials. Dried, waste chromic sulfate can be packed in multi-wall moisture resistant paper bags and in fiber drums.[2055] Chromic fluoride is shipped by Allied Chemical in 100- and 300-pound steel drums and it is believed that these are also adequate for the transportation of chromic fluoride wastes.[1980] The International Air Transport Association (IATA) classifies solid chromic fluoride as "other restricted articles"; Class B; no label is required. Chromic fluoride solutions are classified by the IATA as corrosive liquids, requiring a white label. These materials should be stored in areas separate from food stuffs. The use of outer protective clothing, rubber gloves and dust controlling breathing equipment is recommended for personnel handling open containers of this material to prevent the possibility of burns and skin lesions.

All personnel and supervisory staff that deal with these types of compounds should be well instructed in the precautions that must be undertaken to prevent hazardous exposure to these materials. These same precautions are, of course, applicable to any procedures or waste management techniques designed to reprocess, repurify or reconcentrate these materials for reuse in the future.

Disposal/Reuse

Hazleton Laboratories has recommended a level of 0.001 mg/m^3 for trivalent chromium compounds in air which one could safely be exposed to continuously without any hazard. The United States Public Health Service has established a limit of 0.05 mg/l (ppm) for hexavalent chromium in drinking water.[1752] But this value is based upon the lowest concentration that could be analytically determined at the time that it was established in 1946. At present, the level of chromium that can be tolerated by man for a lifetime without adverse effects on health is unknown and no information was found concerning the disposal of trivalent chromium compounds in the soil.

5. EVALUATION OF CURRENT WASTE MANAGEMENT PRACTICES

Precipitation by rendering waste streams alkaline is the only current method for treating trivalent chromium wastes when present in concentrated and reasonably uncontaminated form. There are other various methods of concentrating waste streams in a particular process for reuse of the concentrates, or effluent water purification, but these have virtually no value to a disposal site and they also have been previously discussed in other process evaluation reports submitted in this effort (reverse osmosis, ion exchange, activated carbon adsorption, etc.).

Option No. 1 - Precipitation by pH Adjustment

Soda ash or other alkaline chemicals are added to trivalent chrome or other heavy metal solutions to adjust the pH to about 9.5;thereby precipitating the insoluble heavy metal hydroxide gels. Aluminum sulfate (alum) or other suitable flocculating agents and also often used to aid in precipitation, settling of the gels and clarification of the effluent. Slaked lime must also be added to precipitate insoluble calcium fluoride, a reaction which requires at least 24 hours. The effluent is neutralized before sewering and the resultant sludge is landfilled.[0095] The procedure can be carried out in either batch or continuous processes. Complete equipment systems are available for performing the precipitation on an automated or semiautomated basis. The biggest drawback of this procedure is the removal and disposal of the highly hydrated metal hydroxide sludges. It is not unusual for these sludges to contain upwards of 75 to 80 percent water by volume. Precipitation and settling is normally a slow procedure and with a high volume of effluent it is normally necessary to have settling ponds or lagoons in which to allow the slow coagulation process to function. The clear effluent can be removed and the residual sludge dried. No feasible economic process has yet been developed for the reclamation of valuable metals or other credits from this type of sludge since it often contains other organic and inorganic materials which hinders effective purification and recovery.

Three ultimate disposal options for these sludges are:(1) landfill, (2) incineration, and (3) ocean disposal. Landfill is believed to be,by far,the most prevalent final disposal procedure but the problem of potential contamination of surrounding land or water tables due to the leaching of poisonous materials from the sludge must be considered. Incineration reduces the sludge to an ash residue which can be more easily handled for ultimate disposal but at the same time could also lead to the formation of poisonous soluble metal oxides. Incineration of course requires additional equipment and a combustible fuel source as well as equipment for air pollution control. Ocean disposal is currently being practiced to a considerable degree by municipal waste treatment plants located near the coast where the primary and secondary sludges can be either pumped or barged out to submarine disposal areas. This disposal approach has been the subject of much recent debate and it is likely that it will not long remain one of the significant sludge disposal options. These three sludge disposal options are discussed in greater detail in the profile reports on the chromate and dichromate salts.

Option No. 2 - Dilute Chrome Discharge to Municipal Sewers

The textile and leather tanning industries, the areas of nearly all the consumption of the subject hazardous materials, can both be characterized as relying mainly on municipal sewage treatment systems to handle the greatest proportion of their waste products in dilute effluents.[1601,0087,1989,1990,1991] Some tanneries precipitate chromic hydroxide by pH adjustment. The effluent is then discharged to the sewer and the precipitated solids and sludges are dumped by commercial companies in landfills.[1991]

When discharged to sewers,most trivalent chrome will precipitate in the sewers by sulfides found in the normal types of domestic and industrial sewage. Precipitation of chromic sulfide then occurs in transit to the waste treatment plant and these solids are then removed by the primary sedimentation and screening facilities of the water treatment plant.

It is currently feasible to treat tannery wastes including the chrome content in adequately designed and operated municipal waste water treatment plants where screening, flotation, and neutralization or precipitation are necessary pretreatments. This option is environmentally acceptable only when it is possible to construct adequate facilities in step with the demand on them.

Sludge and Solids from Options 1 and 2

Whether the trivalent chromium is handled in a pH adjustment process or is precipitated as a result of sewering, the end result is a sludge of metal hydroxides or sewage solids containing precipitated chromium compounds. The ultimate disposal of solids from public and private waste treatment still remains a difficult and critical problem. It has been previously discussed in the Profile Report on the chromates and dichromates, as well as numerous studies and reports on the approach to sludge and semi-solid disposal.

Summary of Available Waste Management Options

Precipitation by pH adjustment	Best method especially if easily recycleable nickel carbonate can be recovered.
Diluted discharge to municipal sewers	Adequate if municipal treatment facilities can efficiently remove waste nickel to meet local discharge standards.

6. APPLICABILITY TOWARDS NATIONAL DISPOSAL SITES

It is recommended that a process for treating concentrated trivalent chromium wastes be included in the design of a National Disposal Site but not for the compounds in this Profile Report. The waste handling characteristics of the tanning and textile industries that create these waste materials are such that no waste stream segregation is being performed in order to capture these materials in concentrated form for transport to a National Disposal Site. In addition, the procedures currently being used either in the on-site industrial treatment plants and the municipal water treatment plants can be designed to adequately manage the chromic sulfate and chromic fluoride waste discharges as they are believed to currently exist. The facility that is recommended for a National Site should be used for various heavy metal, concentrated wastes which could occasionally need handling. These would include other Cr compounds, Zn, Ni, Pb, Hg, Cu and others.

It is, of course, necessary for those with authority in private and municipal waste water treatment to keep pace with the demands that these waste chromium compounds and other waste materials place upon the waste treatment plants. It is also reiterated that the greatest problem facing the current types of waste treatment previously discussed is that of disposing the solids and sludge material from the various and private municipal treatment plants.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chromic Sulfate

IUC Name ________

Common Names Chromium Sulfate, Wool Mordant

Structural Formula

$Cr_2(SO_4)_3$ (1)

Molecular Wt. 392.18(1) Melting Pt. ________ Boiling Pt. ________

Density (Condensed) 3.012(1) @ ____° ____ Density (gas) ________ @ ____° ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____° ____ @ ____° ____ @ ____°

Flash Point ____° Autoignition Temp. ____°

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water Both soluble and insoluble* Hot Water ________ Ethanol slightly soluble

Others: ________

Acid, Base Properties ________

Highly Reactive with ________

Compatible with ________

Shipped in ________

ICC Classification ________ Coast Guard Classification ________

Comments *Some chromic salts exist in two forms, a soluble and an insoluble modification Basic chromic sulfates existing varying mixtures and no one set of physical data is representative of the class of compounds.

References (1) 1570

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chromium Cyanide

Structural Formula

$Cr(CN)_2$ or $Cr(CN)_3$

IUC Name

Common Names

Molecular Wt. Melting Pt. Boiling Pt.

Density (Condensed) @ ° Density (gas) @ °

Vapor Pressure (recommended 55 C and 20 C)

@ ° @ ° @ °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lower Upper

Explosive Limits in Air (wt. %) ower Upper

Solubility

Cold Water Hot Water Ethanol

Others:

Acid, Base Properties

Highly Reactive with Decomposes in air.

Compatible with

Shipped in

ICC Classification Coast Guard Classification

Comments $CrCl_3 + 3KCN$ $Cr(CN)_3$ (a green blue precipitate in excess KCN)(1)
$CrCl_2 + 2KCN$ $Cr(CN)_2$ (a white precipitate)(1)

References (1) 2055

HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Chromic fluoride

IUC Name

Common Names Chromium trifluoride

Structural Formula

CrF_3(1)

Molecular Wt. 108.99(1) Melting Pt. 1000 C(1) Boiling Pt. sublimes(1)

Density (Condensed) 3.8(1) @ ° Density (gas) @ (1100-1200)

Vapor Pressure (recommended 55 C and 20 C)

@ ° @ ° @ °

Flash Point ° Autoignition Temp. °

Flammability Limits in Air (wt %) Lowe Upper

Explosive Limits in Air (wt. %) Lower Upper

Solubility

Cold Water insoluble* Hot Water Ethanol insoluble

Others: slightly soluble acids; soluble HF and HCl

Acid, Base Properties

Highly Reactive with

Compatible with

Shipped in

ICC Classification IATA Classification Other resricted no label(as solid)

Comments 1) inorganic fluorides generally toxic and emit toxic fumes on heating,
2) or acid contact

*$CrF_3 \cdot 4H_2O$:S = 44.8% at 25C; soluble in hot water(1)

$CrF_3 \cdot 3H_2O$:S = 2.63% at 25C; 3.46% in hot water(1)

References (1) 1570
(2) 0766

PROFILE REPORT

Manganese (499)

1. GENERAL

Production and Use

Although the United States possesses reserves of manganese ores (greater than 35 percent Mn content) and manganiferous ores (5 to 35 percent Mn content), direct importation of ores is considered more economical than mining, so that the domestic production accounts for only 8 percent of the annual consumption (256,000 short tons ore mined vs. 3,045,000 short tons consumed in 1968).[1288] Imports account for the balance. There is virtually no recycling of used metal, although the United States Bureau of Mines has invested a great amount of experimental effort over a period of time in attempts to reclaim the 7 to 8 percent manganese contained in spent slag from basic open-hearth furnaces.[0101,0102,0103,0108,0118,0120]

Manganese is chemically and metallurgically similar to iron, and it is won from its ores by smelting in a blast furnace in a manner analogous to the smelting of iron.[1433] Occasionally low grade ores are beneficiated by leaching with sulfuric or nitric acid.[1287]

Over 90 percent of the manganese consumed is alloyed with iron and used as an additive in the production of steel.[1288,0642,1433] The most popular alloy is ferromanganese (80 percent Mn-20 percent Fe). Others include spiegeleisen (20 percent Mn-bal. Fe, C) and silicomanganese (65 to 70 percent Mn-15 to 20 percent Si). Ferromanganese and spiegeleisen are produced mostly in blast furnaces, while silicomanganese is produced in electric arc furnaces. These alloys are made and sold by many of the larger chemical companies, e.g., Foote Mineral Co., Kerr-McGee Corp., and Union Carbide Corp. Many steel companies, including Bethlehem Steel and U.S. Steel, produce their own.[1433]

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Approximately one percent of the manganese consumed (27,000 tons of ore annually) is used in the smelting of pig iron. Welding rods and fluxes account for an insignificant amount in terms of quantity, but may nevertheless pose a health hazard.[0277,0642]

The chemical industry accounts for approximately 7 percent of the total annual consumption. Most of this is refined electrolytically and converted to synthetic manganese dioxide for the production of dry cell batteries.[1288] A small amount is used as a feed additive to prevent deficiencies in livestock and as fertilizer. The Ethyl Corporation is currently in the preliminary phases of marketing manganese methylcyclopentadienyltricarbonyl as a replacement of lead tetraethyl in gasoline [0642,2128] for cars equipped with catalytic afterburners. Manganese methylcyclopentadienyltricarbonyl is discussed in the profile report on Manganese Methylcyclopentadienyltricarbonyl (502).

Manganese is a common impurity in coal (0.005 to 1 percent), and some is released to the atmosphere when coal is burned.[0642]

2. TOXICOLOGY

Health and Safety Standards

The Threshold Limit Value (TLV) recommended by the American Council of Governmental Industrial Hygienists is 5 mg/m^3 air.[0766] It is likely that this represents a maximum exposure limit rather than a uniformly safe standard, since disease has been reported in workers exposed to this limit. [0277,2114] The State of Pennsylvania requires a short-term maximum limit of 5 mg/m^3 for 30 min.[2112] Chronic symptoms of manganese poisoning were found at levels of 5, 6, 30, and 59 mg/m^3 air.[0277] The 1971 Annual List of Toxic Substances[1312] reports that 11 mg/m^3 by inhalation produced toxic effects in man. Both the central nervous system and the lungs were affected. Similarly, serious chronic symptoms were produced in two manganese steel workers, even though environmental assays showed manganese concentrations ranging from 2.3 to 4.7 mg/m^3 air.

Epidemiology

The only significant mode of entry is by inhalation of dusts and fumes.[2110,2111,2112,2114] The clinical symptoms have been well documented.[0277, 0642,2110,2116] They primarily involve malfunctioning of the central nervous system, probably by enzyme inhibition. Warning and diagnosis is complicated by an incubation period of 6 to 30 days prior to the onset of symptoms. Definitive confirmation of manganism is by urinalysis; manganese is cumulated temporarily in the body and then discharged gradually in μg/ml quantities. $CaNa_2$ EDTA administered intravenously is effective treatment in early stages of disease. Clinical evidence shows a marked increase in urinary concentrations on administration of $CaNa_2$ EDTA, which indicates that $CaNa_2$ EDTA promotes elimination of the metal through the kidneys. A controlled, clinical study of Chilean miners suggests that a positive correlation exists between nutritional deficiency and susceptibility to manganism.

Pulmonary damage and high incidence of pneumonia have been reported among persons living in the neighborhood of manganese steel plants in Great Britain, Norway, Italy, and the U.S.S.R., but none has been reported in the United States.[0277,0642] Laboratory experiments in Great Britain and the U.S.S.R. involving intratracheal injections of manganese oxides in rats have confirmed the clinical evidence.

Inorganic and/or insoluble manganese and manganese salts administered orally are passed virtually unabsorbed. Oral administration of 100 ppm Mn stimulates animal growth, while 600 ppm proves deleterious.[0277]

3. OTHER HAZARDS

Manganese dust is a moderate hazard with respect to explosion.[0277] The minimal explosive concentration is 125 oz/1000 ft^3 and the minimum required oxygen concentration is 15 percent. At 450 C manganese dust will ignite spontaneously.

4. DEFINITION OF WASTE MANAGEMENT PRACTICES

Handling, Storage, and Transportation

On a worldwide basis, industrial manganese poisoning is most prevalent in the mining industry, where the mining, transporting, crushing, and sieving of the ore generate considerable quantities of dust containing manganese mixed with arsenic, lead, cobalt, and nickel.[0277] No special provisions attend the shipment of the ore.

In the manufacturing of ferromanganese, steel, other metallurgical products, and in the chemical industry, waste management involves controlling the quantity of dust emitted to comply with the 5 mg/m^3 Threshold Limit Value.[2112] Standard industrial techniques such as baghouses, electrostatic precipitators, forced ventilation, face masks, and respirators are used to minimize worker exposure.

Disposal/Reuse

Manganese mine tailings contain less than 5 percent manganese and are discarded in the vicinity of the mine.

In steel plants, control of manganese dust is treated as part of the larger problem of general particulate emissions. Steel mill tailings contain 7 to 8 percent manganese, but as yet, despite considerable efforts, means have not been found for reclaiming the manganese economically.[0101,0102,0103,0108,0118,0120] These mill tailings contain almost all the manganese waste generated within the United States. Manganese waste as a component of steel mill tailings is discussed in the profile report on Mill Tailings (276).

Manganese dust collected in manganese plants is disposed of in an unsegregated, uncontrolled manner;[2129,2130] probably by burial in an insoluble form.

The disposal of manganese as it arises from the production and use of manganese methylcyclopentadienyltricarbonyl is discussed in the profile report on Manganese Methylcyclopentadienyltricarbonyl (502).

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

Since the predominant danger with regard to manganese poisoning is by inhalation, the burial of unsegregated, nearly insoluble wastes does not constitute a significant hazard.

Option No. 1 - The Discarding of Manganese Dusts and Mine Tailings in the Vicinity of the Mine. These wastes are insoluble. While the situation nationally, with regard to mine tailings, is in general unsatisfactory, manganese tailings pose no special problems of their own, and comprise a small fraction of the total amount of tailings in existence.[0074] No documentary evidence was found for manganese poisoning among mine workers in the United States. This may be attributable in part to the ever-decreasing size of this industry domestically. 256,000 short tons of manganese ore were mined in the United States in 1968, compared to 302,000 tons in 1967 and 339,000 tons in 1966.[1288]

Option No. 2 - The Burial of Manganese as a Component of Steel Mill Tailings. This procedure is evaluated in the profile report on Mill Tailings.(276)

Option No. 3 - The Collection and Burial of Manganese Dusts at Local Plant Sites. With regard to industrial exposure, waste management practices range from satisfactory to unsatisfactory. In response to several clearly diagnosed cases of manganism from a broad segment of industry,[2112,2114] the Division of Occupation Health, Pennsylvania State Department of Health, undertook an investigation of manganese-using plants within the State of Pennsylvania.[2112] Generally, poor housekeeping and malfunctioning, poorly-maintained equipment combined to create hazardous conditions in many plants. The number of plants not complying with the Threshold Limit Value of 5 mg/m^3 listed on an industry-by-industry basis, has been presented by Tanaka and Lieben (Table 1).[2112]

In each case, compliance would not have been inherently difficult or expensive. The seriousness of the statistics is compounded by the fact that the present TLV is too high, and at best constitutes a ceiling value, rather than a true index of safety.

The situation apparently has not improved markedly in the four years since this study was made.[2129] In 1971, two new cases of manganism were diagnosed in the State of Pennsylvania. In view of the rarity of this disease and the non-specificity of its symptoms, it is probable that more were mis-diagnosed. Pennsylvania may be considered typical of other states.[2129]

These dusts are insoluble, and once they are collected, their burial does not constitute a significant hazard.

With regard to the general public, extensive studies indicate that there is no air or water pollution problem at present.[0642,0768,2107,2108,2109,2118] No documentary evidence was found for manganism among the general public. Spectrographic analyses of the water supplies of the 100 largest cities in the United States indicated a median manganese concentration of 5.0 μg/l (0.005 ppm) and a maximum manganese concentration of 1,100 μg/l (1.1 ppm). The American Water Works Assocation specifies that ideal water should contain a maximum of 0.01 ppm Mn,[2118] while the U.S. Public Health Service regards 1.0 ppm as an acceptable level.[0285] Air pollution studies indicated an average of 0.10 μg/m^3 in one study[0642] and a range of 0.005 to 1.44 μg/m^3 in another.[2106] These findings and recommendations are summarized in Table 2. It is seen that air emissions are well below the recommended levels. Water emissions are also well below the recommended levels, except for several city water supplies which depend on natural ground water. These are found to be boderline acceptable.

6. CONCLUSIONS, RECOMMENDATIONS AND SUITABILITY FOR NATIONAL DISPOSAL SITES

At present, manganese does not constitute a hazard to the general public. There is evidence, however, that current industrial practices may involve exposures of workers to levels which are presently regarded as unsafe. These exposures are in the form of atmospheric dust and constitute a serious industrial health threat, since the current Threshold Limit Value itself is in need of revision downward. The problem is primarily one of dust control and ample technology is presently available to solve it with minimal economic impact.

Manganese mine tailings containing less than 5 percent Mn are not significantly different than other tailings. The suitability of taconite tailings for National Disposal Sites is discussed in the profile report on Taconite Tailings (419).

Similarly, the manganese contained in steel mill tailings is discussed in the profile report on Mill Tailings (276). Although the tailings only contain 7 to 8 percent manganese, they account for almost all the manganese waste generated in the United States.

The inadequacy of dust control within industrial plants is a problem amenable to solution by education and by application of current technology. Manganese and manganese compounds are relatively insoluble and inert unless inhaled, and while some control of their disposal as solid waste would be desirable, burial in an unsegregated manner with other wastes does not constitute a significant hazard. Manganese is therefore not a candidate for a National Disposal Site.

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HAZARDOUS WASTES PROPERTIES WORKSHEET

H. M. Name 499

IUC Name Manganese

Common Names Manganese

Structural Formula

Mn

Molecular Wt. 54.9 (1) Melting Pt. 1260 C (2) Boiling Pt. 1900 C

Density (Condensed) 7.20 g/cc @ 20 C Density (gas) ____ @ ____ ____

Vapor Pressure (recommended 55 C and 20 C)

1 mm @ 1292 C ____ @ ____ ____ @ ____

Flash Point ____ Autoignition Temp. 450 C

Flammability Limits in Air (wt %) Lower moderate (as dust) Upper ____

Explosive Limits in Air (wt. %) Lower 125 oz/1000 ft^3 (as dust) Upper <15% O_2

Solubility

Cold Water insoluble Hot Water insoluble Ethanol insoluble

Others: sol. acids, insol. bases

Acid, Base Properties slightly basic

Highly Reactive with acids

Compatible with metals, oxides

Shipped in no special requirements

ICC Classification not classified Coast Guard Classification ____

Comments fumes and dust hazardous if inhaled

References (1) 766
(2) 766
(3)

TABLE 1

MANGANESE AIR EMISSIONS IN INDUSTRIAL PLANTS

Type of Industry	Total No. Plants	No. Above TLV	% in Violation
Steel	24	2	8.4
Nonferrous metals	11	0	0
Metal manufacturing	22	2	9.1
Ceramics, brick, etc.	6	1	16.7
Chemical manufacturing	5	3	70.0
Processing of ore or ferromanganese	4	4	100.0
Miscellaneous	3	0	0
Total	75	12	

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TABLE 2

GENERAL PUBLIC EXPOSURE TO MANGANESE AIR AND WATER EMISSIONS

	Mean (or Median)	Range	Recommended
Air emissions	0.10 μg/m^3 [0642]	0.005-1.44 μg/m^3 [2106]	5,000 μg/m^3 [0766]
Water emissions	0.005 ppm[0285]	0-1.1 ppm[0285]	1.0 ppm[0285]

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PROFILE REPORT

Manganese Methylcyclopentadienyltricarbonyl (502)

1. GENERAL

Production

There is one producer of manganese methylcyclopentadienyltricarbonyl ($CH_3C_5H_4Mn(CO)_3$) in the United States, the Ethyl Corporation, which produces an undisclosed amount at its Orangeburg, South Carolina plant.(2128,2177) Ethyl owns at least six patented processes for the production of $CH_3C_5H_4Mn(CO)_3$ [1433] of which only one is currently in use.[2177] Methylcyclopentadiene is reacted with metallic sodium to form methylcyclopentadienylsodium. This in turn is reacted with manganese chloride to yield biscyclopentadienylmanganese plus sodium chloride. The mixture is scrubbed with oil and water and the resultant pure biscyclopentadienylmanganese is reacted with carbon monoxide to yield the manganese methylcyclopentadienyltricarbonyl. The final product contains traces of manganese cyclopentadienyltricarbonyl, which are considered acceptable.[2174]

Use

At present, $CH_3C_5H_4Mn(CO)_3$ is used as an additive to distillate type fuel oils to improve combustion under the trade name CI-2. The utilities industries have found it particularly useful for reducing the opacity of their stack gases.[2176] As a fuel component it is combusted completely to the manganese oxides.

The Ethyl Corporation hopes to expand its use considerably as an antiknock additive to gasoline (trade name AK-33X) to replace lead tetraethyl.[2128] It is anticipated that, beginning with the 1975 model year, cars will have to be equipped with catalytic afterburners to satisfy the projected pollution requirements. At present, all proposed catalysts are poisoned by lead, but not by manganese; hence the interest in $CH_3C_5H_4Mn(CO)_3$. Projected additions range from 0.025 to 0.05 g Mn/gal gasoline as Mn metal, compared to the present addition of 2.3 to 2.4 g Pb/gal gasoline as Pb metal. At

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\$2.10/lb in tank car quantities, however, it is not economically competitive with lead tetraethyl at present.[2175]

It has been experimentally determined[2176] that all Mn that would be emitted from automobile exhausts would be in the form of the oxides. The $CH_3C_5H_4Mn(CO)_3$ is unstable with respect to sunlight, and decomposes slowly to a brown flocculent material. No chemical analysis has ever been performed on these decomposition products.[2176,2177]

2. TOXICOLOGY

Health and Safety Standards

The HEW 1971 Annual List of Toxic Substances[1312] reports that 0.12 mg/m^3 of manganese cyclopentadienyltricarbonyl produced symptoms of pulmonary disorder and disorders of the central nervous system in man. The mode of entry was by inhalation. Since the methylcyclopentadienyltricarbonyl is chemically similar to the cyclopentadienyltricarbonyl, it is reasonable to assume that manganese methylcyclopentadienyltricarbonyl would produce the same effects.

Epidemiology

Since the reported symptoms of manganese cyclopentadienyltricarbonyl poisoning are the same as those reported for manganese metal poisoning, i.e., pulmonary disorders and impairment of the central nervous system, it is reasonable to assume that the mechanisms are similar. It is generally believed that manganism is caused by enzyme inhibition in the central nervous system. $CaNa_2$ EDTA administered intravenously provides relief in the early stages of disease; prolonged chronic illness is essentially incurable. The epidemiology of manganese poisoning is discussed more fully in the profile report on Manganese (499).

On the basis of experimental evidence,[2197,2198] Russian workers suggest an LD50 of 150 mg/kg for white mice and an LD50 of 80 mg/kg for white rats for manganese cyclopentadienyltricarbonyl. Administration was by direct insertion into the gastrointestinal tract. In addition to the symptoms of manganism, extensive hemolysis was found in the subject animals. It is postulated that this was due to cyclopentadiene which split off the original molecule.

3. OTHER HAZARDS

Manganese methyclopentadienyltricarbonyl is flammable with a flash point in excess of 200 F.[2176] It decomposes slowly in sunlight to unidentified products whose potential hazards cannot be evaluated until such time as they are characterized.

4. DEFINITION OF WASTE MANAGEMENT PRACTICES

Handling, Storage, and Transportation

Manganese methylcyclopentadienyltricarbonyl is a flammable liquid of relatively lower vapor pressure (0.08 torr at 20 C) and high flash point (greater than 200 F).[2176] As a component of gasoline, the maximum anticipated concentration is 0.20 g/gal or 0.05 g Mn/gal gasoline as Mn metal.[2128] $CH_3C_5H_4Mn(CO)_3$ must be stored in opaque containers, for it is decomposed by sunlight to a brown flocculent material of unknown composition.[2174,2177] Otherwise, it remains quite stable below its flash point, which is in excess of 200 F. It is shipped in steel drums or tank cars,[2175] suitably labeled as a Class B poison, flammable liquid.

Disposal/Reuse

When distillate fuels or gasoline containing $CH_3C_5H_4Mn(CO)_3$ are combusted, the only manganese compounds released are mixtures of the oxides.[2128] Field studies of stack emissions from stationary sources indicated concentrations of 0.1 to 0.2 $\mu g/m^3$ 1,000 ft downwind (compared to 0.01 to 0.2 $\mu g/m^3$ background) and 0.03 to 0.05 $\mu g/m^3$ 1,500 ft downwind (compared to 0.02 $\mu g/m^3$ background). On-site soil samples contained 12 to 109 ppm Mn, while off-site soil samples contained 28 to 61 ppm Mn. The samples may have been contaminated with indigenous coal dust which runs 1,000 ppm Mn.[2194]

The waste products from the manufacture of $CH_3C_5H_4Mn(CO)_3$ consist of an oil soluble portion and a water soluble portion. There are no volatiles as such.[2177] The oil soluble portion, which undoubtedly contains some manganese, is incinerated. The stack gases are not monitored for manganese, although requirements imposed by the State of South Carolina with regard to opacity, SO_2, and oxides of nitrogen are being met consistently. The water soluble stream, which is believed to contain the bulk of the waste manganese, is fed into a nearby stream. Manganese concentrations in the plant influent and effluent are 2.6 mg/l and 4.2 mg/l as Mn metal, respectively.

5. EVALUATION OF WASTE MANAGEMENT PRACTICES

As an additive to gasoline or other fuels, $CH_3C_5H_4Mn(CO)_3$ compares very favorably to lead tetraethyl. It has a lower vapor pressure (0.08 torr vs. 0.47 torr at 20 C), a lower anticipated concentration in gasoline (0.20 g/gal vs. 3.75 g/gal for $Pb(C_2H_5)_4$), and is probably somewhat less toxic (symptoms induced in man at 0.12 mg/m^3 vs. a TLV for $Pb(C_2H_5)_4$ of 0.075 mg/m^3). Its handling, storage, and transportation under its classification as a Class B poison, flammable liquid, are adequate at present and for the foreseeable future.

Its susceptibility to decomposition under the action of sunlight is widely known, and the producer and users exercise care that it not be exposed. The decomposition products have not been characterized, however, so any possible hazards associated with decomposition cannot be evaluated at this time.[2193,2195,2174,2176,2177]

Currently, the addition of 2.3 to 2.4 g Pb/gal gasoline as $Pb(C_2H_5)_4$ provides a maximum urban air concentration of 2.3 $\mu g/m^3$,[2106] or 1/100 of the TLV for Pb.[0766] If it is assumed that lead tetraethyl is replaced completely by manganese methylcyclopentadienyltricarbonyl in the concentration of 0.025 to 0.05 g Mn/gal gasoline,[2128] then the Mn air level from automobile exhausts will be approximately fifty times less than the present Pb level, or 1/1250 of the TLV for Mn. It is unlikely that this would present a health hazard, notwithstanding the apparent lack of safety margin in the present TLV of 5 mg/m^3 for Mn.

The Chemistry and Physics Branch of the U.S. Environmental Protection Agency[2195] is sponsoring an experimental study of $CH_3C_5H_4Mn(CO)_3$ additions to gasoline, which will be conducted by the Dow Chemical Company. Initial results are expected in November 1972. Similarly the Chemistry and Physics Branch will soon begin a joint study with the U.S. Navy on the consequences of $CH_3C_5H_4Mn(CO)_3$ additions to jet fuel used in engine overhauling and testing.

Production of Manganese Methylcyclopentadienyltricarbonyl

There are two waste streams associated with the production of manganese methylcyclopentadienytricarbonyl by the Ethyl Corporation in its Orangeburg, South Carolina facility: (A) an oil soluble stream; and (B) a water soluble stream.[2177] These streams are treated individually and there are several options available for each one.

Option No. A1 - Incineration of the Oil Stream and Venting to the Atmosphere. This is the present procedure. Any organic manganese compounds present are converted to the oxides. There is no monitoring of manganese emissions, although state requirements with regard to opacity, SO_2, and oxides of nitrogen are being met consistently. It is necessary to determine the emission level of manganese before an evaluation can be made with regard to the adequacy of this option.

Option No. A2 - Incineration of the Oil Stream and Wet Scrubbing of the Exhaust Gases. If it is determined that manganese emissions from the incinerator exceed the threshold limit value of 5 mg/m^3, a wet scrubber could be installed to bring the air emissions to an acceptable level. The effluent from the scrubber could be combined with the water soluble waste stream.

Option No. B1 - Discharging the Water Stream Into the Local River. This is the present procedure. It is probably unsatisfactory since the effluent runs 4.2 mg Mn/l and the U.S. Public Health Service recommends a maximum Mn concentration of 1.0 ppm (1 mg/l). However, the plant influent which is derived from ground water, runs 2.6 mg/l, which is also above the USPHS standard, so probably little practical effect results from the increase in Mn concentration as the water passes through the plant.

Option No. B2 - Precipitating the Manganese in a Settling Pond Prior to Discharging into the Local River. If the manganese contained in the effluent is indeed objectionable, it can be precipitated quite easily by temporary storage of the effluent in a settling pond in which the pH is adjusted within the range 8.5 to 9 by the addition of lime. Water of this pH would meet USPHS specifications with regard to pH and would be essentially manganese-free.

6. CONCLUSIONS, RECOMMENDATIONS AND SUITABILITY FOR NATIONAL DISPOSAL SITES

At present, manganese methylcyclopentadienyltricarbonyl does not constitute a hazard or threat to the general public. The manganese oxides resulting from its combustion as a gasoline additive would not constitute an air pollution problem, and would represent a considerable improvement over the combustion products of the lead tetraethyl currently in use.

The handling, storage, and transportation of $CH_3C_5H_4Mn(CO)_3$ are adequate at present and for the foreseeable future, providing the manufacturer's admonitions to avoid exposure to sunlight are obeyed. The photochemical decomposition of $CH_3C_5H_4Mn(CO)_3$ has been observed, but not characterized. There is a small, but finite chance that poisonous manganese carbonyls are evolved.[2181,2195] It is recommended that the decomposition products be characterized in a laboratory setting.

It is recommended that a determination be made of manganese air emissions resulting from the incineration of the oil soluble waste stream at the Ethyl Corporation's production facility at Orangeburg, South Carolina. If it is found that the emissions exceed recommended levels, a wet scrubbing unit should be installed to remove them. The effluent from the scrubbing unit could then be mixed with the water soluble waste stream.

Since the plant influent at 2.6 mg Mn/l is already considerably higher than the U.S. Public Health Service recommended level of 1.0 mg/l, it is doubtful if raising it to 4.2 mg/l does much additional harm. These values have already been reported to the U.S. Army Corps of Engineers and the Environmental Protection Agency.[2177] If it is desired to reduce the Mn content, the addition of lime in a settling pond would prove a simple expedient. The precipitation of the manganese would not involve the creation of any volatiles.

Manganese methylcyclopentadienyltricarbonyl can be handled quite adequately at the industrial level and is therefore not a candidate for National Disposal Sites.

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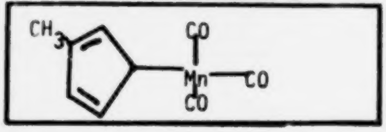
HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name 502

IUC Name Manganese methylcyclopentadienyltricarbonyl

Common Names CI-2, AK-33X

Structural Formula



Molecular Wt. 218 (1) Melting Pt. 1.5 C (2) Boiling Pt. 228.6 C

Density (Condensed) 1.3884 gl/ml @ 20 C Density (gas) ____ @ ____ (extrapolated)

Vapor Pressure (recommended 55 C and 20 C)

0.08 mm Hg @ 20 C 9.3 mm Hg @ 100 C ____ @ ____

Flash Point > 200F Autoignition Temp. ____

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water insoluble Hot Water insoluble Ethanol soluble

Others: most organic solvents

Acid, Base Properties ____

Highly Reactive with ____

Compatible with ____

Shipped in steel drums (1 gal, 5 gal, 55 gal) tank cars (4000, 6000, 8000 gal)

ICC Classification Class B poison, flam. liquid Coast Guard Classification ____

Comments decomposes in sunlight to unidentified products

References (1) 2176
(2) 2176
(3)

PROFILE REPORT

Hydrazoic Acid (528)

1. GENERAL

Hydrazoic acid is a colorless liquid, of sharp, irritating odor with a boiling point of about 37 C. It is highly poisonous with a toxicity about equal to that of hydrogen cyanide. Liquid hydrazoic acid is very dangerous to handle owing to the ease with which it explodes.

Hydrazoic acid is a weak acid like acetic acid. It reacts with zinc, iron, magnesium, and aluminum to form azides with evolution of hydrogen. A small amount of ammonia is also produced, due to the reduction of hydrazoic acid. Hydrazoic acid also reacts with copper, silver and mercury, but in a different way. It forms azides without loss of hydrogen and a considerable amount of hydrazoic acid is reduced to ammonia or hydrazine and free nitrogen. Hydrazoic acid, like nitric acid, oxidizes hydrogen sulfide to form sulfur:

$$HN_3 + H_2S \rightarrow S + N_2 + NH_3$$

When mixed with hydrochloric acid it forms a solution resembling nitro-hydrochloric acid in its properties and is capable of dissolving noble metals.

There are two methods for the manufacture of hydrazoic acid or its salts. One is based on the action of nitrous acid on hydrazine:

$$N_2H_4 + HNO_2 \rightarrow HN_3 + 2H_2O$$

An excess of nitrous acid decomposes hydrazoic acid in accordance with the equation as follows:

$$HN_3 + HNO_2 \rightarrow N_2 + N_2O + H_2O$$

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This is a quantitative reaction and is used to destroy waste azides.

Nitrous esters may be employed for the manufacture of hydrazoic acid, e.g., ethyl nitrate in the presence of sodium hydroxide.

$$N_2H_4 + C_2H_5NO_2 + NaOH \rightarrow NaN_3 + C_2H_5OH + 2H_2O$$

With this reaction sodium azide is formed instead of hydrazoic acid. The second method of manufacture is based on the action of nitrous oxide on sodium amide.[1662,2171]

Even in laboratory quantities, hydrazoic acid is not normally sold or shipped.[1411] In the laboratory, sodium azide is reacted with sulfuric acid and the resultant hydrazoic acid purified by distillation.[2171]

The physical/chemical properties of hydrazoic acid are summarized in the attached work sheet.

2. TOXICOLOGY

Vapors of hydrazoic acid irritate the respiratory tract, particularly the nasal mucosa, and its aqueous solution burns the skin. Hydrazoic acid interferes with the oxidation-reduction processes in the human body causing injury to kidneys and spleen. Headache, weakness, and unsteadiness have also been reported following continued industrial exposure. The chief physiological effect of azides is a marked lowering of the blood pressure with an accompanying rise in heart beat and an increase in respiration rate. Concentration in air within the range 0.5 to 7.0 mg/m^3 evoke marked symptoms of intoxication. The toxic effect may be delayed; symptoms appearing the day following exposure.[2171] A threshold limit for hydrazoic acid has not been established by the American Conference of Government Industrial Hygienists.[0225]

3. OTHER HAZARDS

Liquid hydrazoic acid explodes on heating to 100 C in a tube. An explosion may also occur either on rapid cooling or handling the liquid under vacuum or by passing compressed oxygen into a vessel containing liquid hydrazoic acid. In dilute aqueous solution hydrazoic acid is stable and not liable to decompose even on long boiling. However, a 17 percent aqueous solution of hydrazoic acid can probably detonate. Gaseous hydrazoic acid is liable to non-explosive decomposition above 250 C. At 33 C its half-life is 12 min. Hydrazoic acid decomposes when exposed to ultraviolet light.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Hydrazoic acid in aqueous solution dissolves iron, zinc and copper with formation of the azide, nitrogen and ammonia, but glass equipment is satisfactory for handling hydrazoic acid. When requried as hydrazoic acid instead of as one of the salts of hydrazoic acid, the acid is usually prepared at the location where it is to be used.[2171] No commercial source for hydrazoic acid exists, and there are no regulations permitting its shipment.

The recommended maximum concentrations of hydrazoic acid released to the environment from waste disposal processes are as follows:

Contaminant and Environment	Maximum Recommended Concentration	Basis for Recommendation
Hydrazoic acid released to the atmosphere	0.005 mg/m^3/24 hrs	0.01 of minimum level that produces symptoms of intoxication.[2171]
Hydrazoic acid released to streams	1 µg/l	48-hr median tolerance limit for bluegills.[0536]

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Hydrazoic acid as a waste will not be encountered in large quantities, but a satisfactory method for its destruction exists. An excess of nitrous acid decomposes hydrazoic acid in accordance with the following equation:

$$HN_3 + HNO_2 \rightarrow N_2 + N_2O + H_2O$$

This reaction is accomplished by diluting the hydrazoic acid with 500 times its weight of water, slowly adding 12 times its weight of a 25 percent solution of sodium nitrite, agitating, and then slowly adding 14 times its weight of a 36 percent solution of nitric acid or glacial acetic acid. A red color produced on addition of ferric chloride solution indicates azide to be present; more time or additional reagents are required to effect complete destruction of azide.[1147,2169] After pH adjustment to 6.0 to 9.0, the reacted solution is diluted to a nitrite and nitrate concentration of less than 450 ppm, a typical maximum allowable concentration in an effluent being discharged to a storm sewer or stream.[0536]

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

The difficulty encountered in shipping hydrazoic acid and the limited quantity used indicates that it is probably not a likely candidate for a National Disposal Site. The treatment facilities that will be available at a National Disposal Site will permit easy treatment of hydrazoic acid, if ever required. The only facilities required are for diluting, addition of chemicals, and mixing.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

H. M. Name Hydrazoic Acid

IUC Name Hydrazoic Acid

Common Names Azoimide

Structural Formula

NH_3

Molecular Wt. 43.03 Melting Pt. -80 C Boiling Pt. 37 C

Density (Condensed) ____ @ ____ ° ____ Density (gas) ____ @ ____ ° ____

Vapor Pressure (recommended 55 C and 20 C)

____ @ ____ ° ____ @ ____ ° ____ @ ____ °

Flash Point ____ ° Autoignition Temp. ____ °

Flammability Limits in Air (wt %) Lower ____ Upper ____

Explosive Limits in Air (wt. %) Lower ____ Upper ____

Solubility

Cold Water 2.14 ml/100 ml Hot Water 0.85 ml/100 ml Ethanol 6.925 gm/100 ml

Others: ____

Acid, Base Properties Weak acid, K = 2.8 x 10^{-5}

Highly Reactive with reducing agents, iron, zinc, copper

Compatible with hydrocarbons, glass

Shipped in not normally shipped

ICC Classification ____ Coast Guard Classification ____

Comments ____

References (1) 1416

APPENDIX C - NUCLEAR PROFILE REPORTS

PROFILE REPORT

Cesium-134, Cesium-137 (Barium-137m)

1. GENERAL

Introduction

Cesium-134 and cesium-137 are both radioactive isotopes principally produced by the fission of uranium and plutonium. Cesium-134 has a fission yield of 8 percent and cesium-137 a fission yield of 6 percent. Cesium-134 has a half-life of 2.05 years and emits both beta particles and gamma rays. Cesium-134 is transformed by beta decay into barium-134 which is a stable element. Cesium-137 has a half-life of 30 years and emits only beta particles. Cesium-137 is in radiation equilbrium with its short half-lived daughter (2.6 minutes), barium-137m. Barium-137m, in turn, is transformed by isometric transition (decay from an excited metastable state to a lower state) into barium-137 which is a stable element.

Cesium-137, because of its long half-life and high fission yield, is one of the most important fission products produced in nuclear reactors. The only fission product of comparable importance is strontium-90. The importance of cesium-137 is realized by the fact that,together with its daughter barium-137m, they account for 10 percent of the total fission product activity in nuclear reactor wastes after 1 year, and for 52 percent of the activity after 10 years. Cesium-134 is also of significance due to its high fission yield (8 percent) and large specific power (20 watts/gram).

The projected growth in the production of cesium-134 and cesium-137 will parallel that of the civilian nuclear power program. Present projections indicate that the total installed capacity of nuclear power plants will grow by a factor of 60 between 1970 and 1985.[2148] Projected annual production figures from the civilian nuclear power programs for these two isotopes to the year 2020 for light-water and fast-breeder reactor fuels

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are attached (Tables 1 and 2). The expected total accumulated radioactivity of cesium-137 from the year 1970 to 2020 in millions of curies is:[0705]

Year	Radioactivity (megacuries)
1970	5
1980	1,280
1990	6,540
2000	15,600
2020	29,400

Annual production figures for the nuclear weapons program were not available.

Manufacture

Cesium-137 is produced directly by the fission of uranium or plutonium. The fission reaction results from the neutron bombardment or spontaneous decomposition of the nucleus. The fission reaction is:

$$_{92}U^{235} + {}_{o}n^{1} \rightarrow {}_{55}Cs^{137} + {}_{37}Rb^{96} + 2{}_{o}n^{1}$$

Cesium-134 is also produced in the fission reaction. Presently, both isotopes are produced in thermal power reactors by the fission of uranium. Civilian nuclear power plants are the major producers and a smaller amount is produced at AEC facilities. At the present time there are 22 nuclear power plants in operation with an additional 104 being built or planned.[2151] In the future, they will also be produced in fast breeder reactors by the fission of plutonium.

Uses

Cesium-137 is used as a radiation source for both industrial and medical equipment. Cesium-137 is used for radioisotope gauges and in industrial radiographic units. It is also used in medical teletherapy units and accounts for 7 percent of the worlds total. At present, cesium-137 is obtained from waste streams in the Richland, Washington, chemical separations plant and is distributed through the Oak Ridge National Laboratory, Isotopes Sales Department. In the future, when its production is warranted by market demands, it could be available in large quantities from commercial firms operating chemical reprocessing plants. The AEC revenue from the distribution of cesium-137 through the fiscal years 1968 to 1971 is [2151]:

Year	Revenue (Dollars)
1968	83,000
1969	42,000
1970	24,000
1971	59,000

These figures illustrate the fluctuating nature of the commercial market for cesium-137. Cesium-134 has very limited commercial use.

Sources and Types of Wastes

The primary source of cesium-134 and cesium-137 waste streams are generated at the spent reactor reprocessing plants. They are primarily contained in the aqueous effluent from the reprocessing step. The range of chemical compositions of the various types of waste streams obtained from the reprocessing step have been tabulated, [0715] and in all cases are primarily aqueous solutions of inorganic nitrate salts. The activity of cesium-134 and cesium-137 products in the spent reactor wastes at two different time periods is attached (Tables 3 and 4). They are also found in the secondary waste streams generated at fuel reprocessing facilities. The activity in these wastes is quite low (less than a tenth of a curie per gal).

Physical and Chemical Properties

The physical and chemical properties of cesium-134 and cesium-137 are included in the attached worksheets. Cesium is a member of the highly electropositive alkali metal group. In its compounds, cesium has an oxidation state of +1 and is extremely reactive chemically. It is a relatively volatile metal, melting at slightly above room temperature (29.5 C) and boiling at 690 C. Most of the salts of cesium are insoluble, however, the chloroplatinates are soluble in water.

2. RADIATION HAZARD

Cesium-134 and cesium-137 are moderately dangerous radioactive materials. The effects of their radiation are primarily dependent on the amount of radiation and the portion of the body affected. The effects of acute whole-body radiation exposure are: (1) 0 to 25 rem, no detectable clinical effects; (2) 25 to 200 rem, delayed effects and possible shortened life expectancy of 1 percent; (3) 200 to 600 rem, possible premature death; (4) greater than 600 rem, death. These effects are for a single large dose of radiation or a series of substantial doses in a short interval of time to the total body. Standards for prolonged exposure over a fifty-year period have defined the single dose limit in terms of the maximum permissible dose accumulated in a period of 13 weeks. The whole body exposure limit is 3 rem per quarter and the accumulated dose limit is 5(N - 18), where N is the individual's age in years. Limits for the thyroid, bone, and other organs have also been defined.[0563]

Following the inhalation of 1 microcurie, the cesium-134 dose in the insoluble form to the lung is 0.56 rem. In the soluble form the dose delivered to the liver following the inhalation of 1 microcurie of cesium-134 is 0.09 rem. The dose delivered to the liver following injection of 1 microcurie into the body via a wound is 0.13 rem. The cesium-137 dose to the lung following the inhalation of 1 microcurie in the insoluble form is 0.46 rem, and in the soluble form the dose to the liver is 0.08 rem. The dose to the liver following the injection of 1 microcurie into the body via a wound is 0.11 rem.

Values of the maximum permissible total body burden of cesium-134 and cesium-137 which are deposited in the total body and produce the maximum permissible dose rate to a particular body organ have been compiled.[0563] For both isotopes the critical organ is the total body and the maximum permissible body burden is 20 microcuries for cesium-134 and 30 microcuries for cesium-137. The above body burden rates can be expressed in terms of the maximum permissible concentration of cesium-134 and cesium-137 in air and water at the continuous exposure rate of 168 hours per week for a period of 50 years. For cesium-134, the maximum permissible concentration in water is 9×10^{-5} microcuries per milliliter and in air 1×10^{-8} microcuries per milliliter. For cesium-137, the maximum permissible concentration in water is 2×10^{-4} microcuries per milliliter and in air 2×10^{-8} microcuries per milliliter.

3. OTHER HAZARDS

Besides its radiation hazard, cesium-134 and cesium-137 are only slightly toxic to the human body if absorbed by inhalation, ingestion, or through the skin.[0766] Their fire hazard is high, since they react with oxidizing materials and can ignite spontaneously in moist air. Their explosive hazard is moderate, but they do react with moisture to liberate hydrogen. Cesium compounds have the same toxicity as cesium unless they contain a more toxic radical.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Since both cesium-134 and cesium-137 are hazardous to man by inhalation, ingestion, or direct radiation exposure, great care must be exercised in their handling. Handling must be set up to prevent excessive exposure to personnel and in fact to prevent any unnecessary exposure. Special procedures and adequate radiation shielding are required in their handling. Both isotopes emit low energy beta particles which cannot penetrate more than 0.09 in. of water or 0.007 in. of lead. To stop their highly penetrating gamma rays high-density shields, such as lead, are required. To reduce their gamma radiation by a factor of 10, approximately 1.5 to 2 in. of lead or 8 to 9 in. of concrete is required. To detect and control personnel exposure all persons working with these materials should wear an external dosimetry device. The commonly used devices are the film badge and the thermoluminescent dosimeters (TLD).

Cesium-134 and cesium-137 should be stored in controlled reservations in specially constructed containers or storage bins. They should be protected by both a primary and a secondary containment barrier. Special monitoring systems and proper warning signs should be located in the general area of the storage facility.

Both cesium-134 and cesium-137 are classified as a transport group III radionuclide by the Department of Transportation, and the rules and regulations governing their transportation are given in the Code of Federal Regulations (CFR) Title 49--Transportation, Parts 170 to 190.[2150] Their content is limited to 3 curies for a Type A package and 200 curies for a Type B package defined in 49CFR173. The limits are increased to 20 to 5,000 curies if their physical form meets the requirements of a special form material. Their release rate is limited to zero under the specified accident conditions for Type A and B quantities.[2150] The allowable release of radioactivity from packages containing large quantities of these isotopes is limited to gases and contaminated coolant containing total radioactivity exceeding neither 0.1 percent of the total radioactivity of the package nor 10 curies under the hypothetical accident conditions prescribed in 49CFR173.

Disposal/Reuse

The disposal of cesium-134 and cesium-137 is governed by the AEC Manual Chapter 0524[0559] and 10CFR20.[2149] Two sets of standards have been established for the permissible radiation exposure in unrestricted areas. One is for the greatest dose received by an individual and the other for the average dose received by the general population. The radiation protection standards for these two groups are attached (Table 5). The standards for the safe disposal of cesium-134 and cesium-137 also define their miximum concentrations in air and water. The safe release of cesium-134 and cesium-137 to the environment in an unrestricted area should not exceed the concentrations in microcuries per milliliter included in this report (Table 6).

The disposal of cesium-134 by release into a sanitary sewage system is limited to 10 microcuries and the disposal of cesium-137 is limited to 100 microcuries. The disposal by burial in the soil at any one location and time is limited to 1,000 microcuries of cesium-134 and 10,000 microcuries of cesium-137.[2149]

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Recovery

Option #1 - Precipitation. Cesium-134 and cesium-137 can be removed from the high-level reactor wastes by precipitating with nickel ferrocyanide. Over 99 percent of the cesium can be removed satisfactorily up to a pH of 10.[0553, 0714] Cesium can also be removed by precipitating with phosphotungstate[0714] or absorbing on alumino-silicate zeolites.[0738] Cesium can be further purified by ion exchange. Cesium is recovered from the other high-level wastes for commercial purposes or for safety reasons.

Option #2 - Scavenging-Precipitation Foam Separation. The removal of cesium-134 and cesium-137 from low-level radioactive waste water by scavenging-precipitation foam separation has been studied by Oak Ridge National Laboratory.[0703] The process consists of two steps:
(1) precipitating in a sludge-blanket clarification step; and
(2) achieving final decontamination in a foam separation column.
The precipitation step includes the use of Grundite clay for the sorption of cesium. The Grundite clay increased the cesium decontamination factor (ratio of initial to final concentration) approximately nine times. The overall decontamination factor for cesium was eight. At present, further development is required to reduce operating costs and increase processing rates.

Option #3 - Scavenging-Precipitation Ion Exchange. In this process final decontamination is obtained by ion exchange columns from the scavenging-precipitation process. The process includes a provision for the recycle of the ion exchange waste to the scavenging-precipitation step. All the removed radionuclides are concentrated in the clarifier sludge. With most ion exchange resins sodium is removed with cesium. Cesium can be separated from sodium by phenolic-base cation exchanges at high pH values. For this process the overall decontamination factor for cesium varied from 100 to 3,000. [0705] The use of ion exchange resins with a scavenging-precipitation step is a fairly simple and efficient means of removing cesium-134 and cesium-137 from low-level radioactive aqueous wastes.

Option #4 - Water Recycle. The water recycle process is used for decontaminating radioactive waste water and recycling the purified water for reuse. This process has been demonstrated at the pilot plant scale by Oak Ridge National Laboratory. [0707] The steps in the process include: (1) clarification by the addition of coagulants; (2) demineralization by cation-anion exchange; and (3) sorption on granular activated carbon. The majority of the cesium is removed by the cation-anion exchange. The cesium overall decontamination factor was 14,000. The method is an improvement to the treat-and-discharge methods, but further work is required until full-scale production use is obtained.

Disposal

Option #1 - Land Burial. Land burial of cesium-134 and cesium-137 wastes, in small concentrations, at approved sites that are acceptable from a geologic and hydrologic standpoint, is an acceptable means of disposal. The cesium-134 and cesium-137 concentrations should not be in excess of 10^4 times their maximum permissible concentrations for the general population in 10CFR20. [2149] All cesium wastes to be disposed of should be in a solid form and encapsulated in a suitable container. Liquid wastes should be solidified, preferably using asphalt, in accordance with the methods described in the Radioactive Waste Solidification report. The burial trenches should be designed not to intercept the ground water table and constructed with a bottom drain and sump for water monitoring. The trenches should be covered with either asphalt or vegetation to prevent infiltration of water. The burial site design, geology, and hydrology should be in conformance with the criteria used in selecting and licensing the present commercial burial sites.[1423] Since land burial has successfully been practiced on a commercial scale, it should be considered as the most satisfactory method of disposing of all dilute concentration of these wastes.

Option #2 - Near-Surface Liquid Storage. Near-surface storage of reactor-produced liquid cesium-134 and cesium-137 wastes in stainless steel tanks encased in concrete and buried underground is not considered as a satisfactory means of disposal. Liquid reactor wastes have been stored in this manner over the past 25 years. The tanks range in size from 0.33 to 1.3 million gal and are generally equipped with devices for measuring temperatures, liquid levels, and leaks. At the present time these tanks are considered as an interim storage technique due to a general lack of confidence in their long-term integrity.[0705] In addition, present regulations require the solidification of all reactor wastes within 5 years following reprocessing.[2149] Therefore, the near-surface storage of liquid cesium-134 and cesium-137 wastes in steel tanks should only be considered as a near-term storage technique and not as a permanent storage or disposal technique.

Option #3 - Near-Surface Solid Storage. The disposal of high-level solidified cesium-134 and cesium-137 wastes in engineered surface facilities offers the best immediate method for disposal of these wastes. The technology for these facilities has been developed and the wastes will be under surveillance and control and can be retrieved, should this be required. The reactor-produced wastes should be solidified and encapsulated in a suitable container (stainless steel). Of the four high-level solidification processes developed, spray solidification offers the best solidified waste characteristics (see Radioactive Waste Solidification report). The wastes will be stored in stainless steel vaults encased in concrete. The vaults will be either air or water cooled. Corrosion of the waste containers will require their periodic replacement. For cesium-137 replacement will be required since its activity is only reduced by a factor of ten in 100 years.

Option #4 - Salt Deposits. This method offers the greatest potential for the disposal of reactor-produced cesium-134 and cesium-137 wastes since bedded salt deposits are completely free of circulating ground waters. This method of disposal has been under study by the Oak Ridge National Laboratory since 1957, and in November of 1970 a committee of the National Academy of Sciences recommended that the use of bedded salt for the disposal of radioactive wastes is satisfactory.[0733] The reactor-produced cesium wastes must be solidified and disposed of in the solid form, encapsulated in a suitable container. The preferred solidification process is spray solidification. The solidified wastes are then buried in rooms carved in the salt deposits approximately 1,000 ft below the ground. The salt is a good heat transmitter, provides about the same radioactive shielding as concrete, and can heal its own fractures by plastic flow. The critical problem is the selection of a site that meets the necessary design and geological criteria. For cesium-137 wastes the life of the mine must extend beyond a few hundred years. Salt deposits should be considered for the disposal of cesium wastes at approved sites that are acceptable from a design and gelogical standpoint. In addition, a method of waste retrieval is required in the event the integrity of the site is destroyed.

Option #5 - Bedrock Disposal. The disposal of liquid cesium-134 and cesium-137 wastes along with other spent reactor wastes in vaults excavated in crystalline rock over 1,500 ft beneath the ground is currently being evaluated by E. I. du Pont de Nemours, at their Savannah River Plant near Aiken, South Carolina.[0894, 1396] The wastes would be stored in six tunnels and once in the tunnels the wastes will seep into the surrounding rock. Located above the crystalline rock is the Tuscaloosa formation, a good source of freshwater, which is separated by a layer of clay that would act as a barrier to the leakage of radioactive wastes. An advisory committee appointed by the National Academy of Sciences recommended abandonment of the project. In May 1972, another National Academy of Sciences panel concluded that bedrock storage provides a reasonable prospect for long-term safe storage, but an unprecedented degree of precise information is needed to decide if and where underground storage vaults should be built. Another method has also been proposed for disposing of liquid wastes by in situ incorporation in molten silicate rock.[2146] At the present time both of these methods are unsatisfactory since sufficient engineering data or exploration has not been completed to verify their suitability. Due to the long half-life of cesium-137, it is doubtful that data could ever be accumulated to prove that the geological characteristics of the site over the next few hundred years are acceptable to ensure the absolute safety of such a disposal method.

Option #6 - Hydraulic Fracturing. The direct disposal of aqueous intermediate-level radioactive wastes into shale formations has been investigated by Oak Ridge National Laboratory.[0709] The method consists of mixing the aqueous wastes with cement and pumping the resulting slurry down a well out into a nearly horizontal fracture in a thick shale formation. Since no additional encapsulation is provided, this method of disposal is not satisfactory.

To summarize, cesium-134 and cesium-137 can be recovered from the high-level reactor waste streams for separate disposal or reuse. The separation of cesium-137 from these waste streams could be required with the introduction of the fast-breeder reactor due to its high heat content and activity (see Radioactive Waste Solidification report). The acceptable method of treatment is solidification and disposal in either salt deposits or near-surface engineered facilities. Cesium should be recovered from the low-level waste streams to minimize the amount directly released to the environment. The recovered cesium should be solidified, preferably using asphalt, and disposed of at approved sites by land burial.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Cesium-134 and cesium-137 are candidates for a National Disposal Site due to their public health hazard and projected growth with that of the civilian nuclear power program. The applicability of the recovery processes to a National Disposal Site are dependent upon whether the reactor-produced cesium wastes are reprocessed at the disposal site or are reprocessed elsewhere and shipped to the site. If reprocessed elsewhere the wastes should be solidified prior to shipment, since the shipment of liquid wastes is extremely dangerous. From a cost and safety viewpoint, it would be desirable to combine the reprocessing plant and the National Disposal Site. Disposal in near-surface engineered facilities offers considerable latitude in the disposal site selection, whereas site selection would be seriously limited with salt mine disposal.

The recommended treatment for low-level cesium waste streams is recovery followed by solidification with asphalt and disposal by land burial. For the high-level, reactor-produced cesium-134 and cesium-137, the recommended processes are:

Process	Order of Preference	Remarks
Near-surface solid storage	First choice	Demonstrated technology; waste under constant surveillance and control and can be retrieved.
Salt beds	Second Choice	Affords permanent disposal without constant surveillance; further development required for a waste retrievel plan and location of an acceptable site.

For each of these processes the wastes should be solidified following the reprocessing step by spray solidification.

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HAZARDOUS WASTES PROPERTIES WORKSHEET

Name Cesium-134

Structural Formula $_{55}Cs^{134}$

Half-life 2.05 years

Type of Decay Negative Beta

Molecular Wt. 134 Melting Pt. 28.5C Boiling Pt. 690C

Density 1.88 gm/cc

Specific Power 20.4 watts/gm

Specific Activity 1,220 curies/gm

Solubility

Cold Water Reacts Hot Water Reacts

Others: Soluble in liquid NH_3

Decay Chain

$$\underset{(2.05y)}{Cs^{134}} \xrightarrow{B^-} \underset{(stable)}{Ba^{134}}$$

Radiation Energy Level & Intensities

Beta: 0.662 Mev (71%)
0.410 Mev (1%)
0.089 Mev (28%)

Gamma: 1.365 Mev (3.4%)
1.168 Mev (1.9%)
0.769 Mev (99%)
0.605 Mev (98%)
0.570 Mev (23%)

Shipping Regulations Classified as a transport group III radionuclide by the Department of Transportation

Comments

References: (1) 0766
(2) 2147
(3) 2150

HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Cesium-137

Half-life 30 years

Type of Decay Negative Beta

Structural Formula $_{55}Cs^{137}$

Molecular Wt. 137 Melting Pt. 28.5 C Boiling Pt. 690 C

Density 1.88 gm/cc Specific Power 0.42 watts/gm

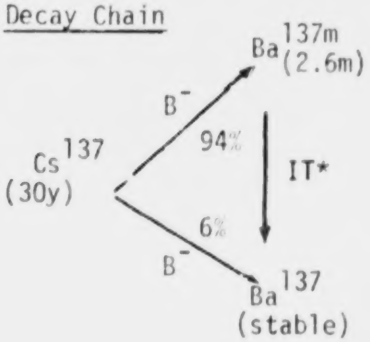
Specific Activity 87 curies/gm

Solubility

Cold Water Reacts Hot Water Reacts

Others: Soluble in liquid NH_3

Decay Chain



Radiation Energy Level & Intensities

Cesium-137

Beta: 1.176 Mev (6%)
0.514 Mev (94%)

Barium-137

Gamma: 0.662 Mev (89%)

*IT = isometric transition

Shipping Regulations Classified as a transport group III radionuclide by the Department of Transportation

Comments

References: (1) 0766
(2) 2147
(3) 2150

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TABLE 1

ANNUAL PRODUCTION OF CESIUM-134 FROM THE CIVILIAN NUCLEAR POWER PROGRAM[0705]

Light-Water Reactor Fuels

Annual Production	Calendar Year					
	1970	1980	1985	1990	2000	2020
grams/year	$.090\times10^5$	5.12×10^5	9.22×10^5	10.4×10^5	8.27×10^5	24.3×10^5
curies/year	$.12\times10^8$	6.66×10^8	12.0×10^8	13.6×10^8	10.8×10^8	31.6×10^8
watts/year	$.123\times10^6$	$.86\times10^6$	1.55×10^6	1.75×10^6	1.39×10^6	4.07×10^6

Fast-Breeder Reactor Fuels

Annual Production	Calendar Year					
	1970	1980	1985	1990	2000	2020
grams/year			$.079\times10^5$	$.48\times10^5$	2.04×10^5	6.13×10^5
curies/year			$.10\times10^8$	$.62\times10^8$	2.66×10^8	8.0×10^8
watts/year			$.11\times10^6$	$.65\times10^6$	2.79×10^6	8.39×10^6

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TABLE 2

ANNUAL PRODUCTION OF CESIUM-137 FROM THE CIVILIAN NUCLEAR POWER PROGRAM [0705]

Light-Water Reactor Fuels

Annual Production	Calendar Year 1970	1980	1985	1990	2000	2020
grams/year	$.064\times10^6$	3.64×10^6	6.56×10^6	7.40×10^6	5.86×10^6	17.3×10^6
curies/year	$.055\times10^8$	3.16×10^8	5.70×10^8	6.45×10^8	5.11×10^8	15.0×10^8
watts/year	$.090\times10^5$	5.11×10^5	9.21×10^5	10.5×10^5	8.26×10^5	23.3×10^5

Fast-Breeder Reactor Fuels

Annual Production	Calendar Year 1970	1980	1985	1990	2000	2020
grams/year			$.45\times10^6$	2.70×10^6	11.5×10^6	34.5×10^6
curies/year			$.39\times10^8$	2.34×10^8	10×10^8	30×10^8
watts/year			$.64\times10^5$	3.8×10^5	16.3×10^5	49.0×10^5

TABLE 3

ACTIVITY OF CESIUM-134 PRODUCED IN SPENT REACTOR WASTE 0705

Light-Water Reactor Fuels
(Fuel Exposed to 33 MWD/Tonne* at 30 MW Tonne)

Fission Products	Grams/Tonne	After 1 year Watts/Tonne	Curies/Tonne	Grams/Tonne	After 10 years Watts/Tonne	Curies/Tonne
Cesium-134	134	1,830	175,200	6	87	8,300
Other Fission Products	34,965	8,170	2,045,000	35,096	943	308,700

Fast-Breeder Reactor Fuels
(Fuel Exposed to 33 MWD/Tonne at 58 MW Tonne

Fission Products	Grams/Tonne	After 1 year Watts/Tonne	Curies/Tonne	Grams/Tonne	After 10 years Watts/Tonne	Curies/Tonne
Cesium-134	116	220	21,200	1	11	1,000
Other Fission Products	34,984	12,780	3,408,800	34,899	755	280,000

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*Tonne is a metric ton of reactor fuel

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TABLE 4

ACTIVITY OF CESIUM-137 PRODUCT IN SPENT REACTOR WASTES 0705

Light-Water Reactor Fuels
(Fuel Exposed to 33 MWD/Tonne* at 30 MW/Tonne)

Fission Products	Grams/Tonne	After 1 year Watts/Tonne	Curies/Tonne	Grams/Tonne	After 10 years Watts/Tonne	Curies/Tonne
Cs^{137} - Ba^{137m}	1,200	555	203,000	980	451	165,000
Other Fission Products	32,900	9,445	2,091,000	34,120	579	152,000

Fast Breeder Reactor Fuels
(Fuel Exposed to 33 MWD/Tonne at 58 MW/Tonne)

Fission Products	Grams/Tonne	After 1 year Watts/Tonne	Curies/Tonne	Grams/Tonne	After 10 years Watts/Tonne	Curies/Tonne
Cs^{137} - Ba^{137m}	1,230	565	207,000	1,000	458	168,000
Other Fission Products	33,770	13,235	3,123,000	33,900	308	113,000

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*Tonne is a metric ton of reactor fuel

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TABLE 5

RADIATION PROTECTION STANDARDS FOR INDIVIDUALS AND POPULATION GROUPS

FOR EXTERNAL AND INTERNAL EXPOSURE[2149]

Type of Exposure	Dose to Individuals at Points of Maximum Probable Exposure (rem per year)	Average Dose to a Suitable Population Sample (rem per year)
Whole body, gonads, or bone marrow	0.5	0.17
Thyroid or bone	1.5	0.5
Bone (alternate standards)	Body burden at 0.003 micrograms of radium 226 or its biological equivalent	Body burden of 0.001 micrograms of radium 226 or its biological equivalent

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TABLE 6

CESIUM-134 AND CESIUM-137 ENVIRONMENTAL RELEASE RATES [2149]

Isotope	Exposure Group	Form	Concentration in Air (microcuries/milliliter)	Concentration in Water (microcuries/milliliter)
Cs-134	Individual	Soluble	$1x10^{-9}$	$9x10^{-6}$
Cs-134	Individual	Insoluble	$4x10^{-10}$	$4x10^{-5}$
Cs-134	Population	Soluble	$.33x10^{-9}$	$3x10^{-6}$
Cs-134	Population	Insoluble	$1.3x10^{-10}$	$1.3x10^{-5}$
Cs-137	Individual	Soluble	$2x10^{-9}$	$2x10^{-5}$
Cs-137	Individual	Insoluble	$5x10^{-10}$	$4x10^{-5}$
Cs-137	Population	Soluble	$.67x10^{-9}$	$.67x10^{-5}$
Cs-137	Population	Insoluble	$1.7x10^{-10}$	$1.3x10^{-5}$

PROFILE REPORTS ON

TRANSURANIUM ELEMENTS

Plutonium-238, Plutonium-239, Plutonium-240, Plutonium-241, Americium-241, Americium-243, Curium-242, Curium-244

1. GENERAL

Introduction

Plutonium, americium, and curium are artificially produced radionuclides that do not exist in nature except for very small amounts of plutonium. These elements are characterized by their high radiotoxicity, long half-life, and ability to fission. Plutonium-239 is the most important among these elements because of its use in nuclear weapons and the place it holds as the key material in the development of fast-breeder reactors for the civilian nuclear power program. Plutonium-239 is readily fissionable with neutrons and one lb of this material is equivalent to about ten billion watt-hours of heat energy.

Americium, curium, and plutonium (except for Pu-241) decay by the emission of high energy, 5 to 6 Mev, alpha particles. Plutonium-241 decays by beta emission to form americium-241. All these elements eventually decay to lead, and the time required is on the order of millions of years. The americium-243 decay chain is attached (Table 1) and the three long-lived isotopes in this chain are: Pu-239, half-life 2.4×10^4 years; U-235, half-life 7.1×10^8 years; and Pu-231, half-life 3.3×10^4 years.

The projected growth in production of these isotopes will parallel that of the civilian nuclear power program. The production of plutonium-239 will increase with the planned introduction of the fast-breeder reactors in the 1980's. Present projections indicate that the total installed capacity of nuclear power plants will grow by a factor of 60 between 1970 and 1985.[2148] The expected total

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accumulated wastes for these isotopes from the civilian nuclear power program to the year 2020 is attached (Table 2). These data assume that 99.5 percent of plutonium is recovered from the spent fuel elements. Annual production figures or accumulated totals for these materials produced as part of the nuclear weapons program were not available.

Manufacture

The transuranium elements are produced in cyclotrons and in thermal power reactors. The majority of the isotopes are produced in civilian nuclear power plants. At the present time there are 22 nuclear power plants in operation with an additional 104 being built or planned.[2151] The present reactor fuel is uranium dioxide. In the future, plutonium dioxide will be used as the fuel in the fast-breeder reactors.

Plutonium. Plutonium-238 is produced in cyclotrons by deuteron bombardment of uranium or in nuclear reactors from neutron bombardment by the reaction:

$$U^{238}(n,2n)U^{237} \xrightarrow{B^-} Np^{238} \xrightarrow{B^-} Pu^{238}$$

Plutonium-238 is also a daughter of Cm-242. Plutonium-239 is produced in extensive quantities in nuclear reactors from natural uranium by the reaction:

$$U^{238}(n,\gamma)U^{239} \xrightarrow{B^-} Np^{239} \xrightarrow{B^-} Pu^{239}$$

Plutonium-240 and plutonium-241 are produced by multiple n-capture from U-238 and Pu-239.

Americium. Americium-241 is a daughter of plutonium-241 and is formed from plutonium-239 in a nuclear reactor by successive neutron capture. Americium-243 is produced by multiple n-capture from U-238 and Pu-239.

Curium. Curium-242 is produced in cyclotrons by the helium-ion bombardment of Pu-239. It is also produced by multiple n-capture from

U-238 and Pu-238 and by the reaction:

$$Am^{241}(n,\gamma)Am^{242} \xrightarrow{B^-} Cm^{242}$$

Cerium-244 is produced by multiple n-capture from U-238, Pu-239, and Am-243.

Uses

Plutonium-238 is used extensively for radioisotopic power devices for space electric power, for radioisotopic heaters, and as an energy source for cardiac pacemakers, heart pumps, and small undersea propulsion systems. Plutonium-239 is used as a fuel in fast-breeder reactors and in nuclear weapons. Presently, plutonium-239 is used in experimental reactors but with the introduction of the fast-breeder reactors in the civilian nuclear power program the requirements for its use will increase rapidly. Curium and americium are used in various national laboratories for research purposes and to produce heavier elements.

Sources and Types of Wastes

The majority of the transuranium elements are produced in nuclear reactors and are contained within the spent fuel elements. The spent fuel elements are reprocessed for the recovery of the usable fission materials (uranium and plutonium) which are refabricated into new fuel elements. Solvent extraction using nitric acid is the means currently used for the first-stage removal of the fissionable materials. Approximately 99 percent of the plutonium is removed during the reprocessing. The other radionuclides along with the unrecovered plutonium are contained in the aqueous effluent from the reprocessing step. The composition of the reactor-produced wastes prior to reprocessing have been tabulated,[0705] and the activity of plutonium, americium, and curium products present in the waste following the reprocessing step are included (Table 3).

Physical and Chemical Properties

The physical and chemical properties of plutonium, americium, and curium are included in the attached worksheets. Plutonium is highly reactive, and in moist air oxidation proceeds rapidly, especially at elevated temperatures. It dissolves in concentrated hydrochloric acid, hydroiodic acid, or perchloric acid with the formation of the Pu^{+3} ion. Plutonium exhibits six allotropic modifications having various crystalline structures whose densities vary from 15.92 to 19.84. Plutonium forms binary compounds with oxygen, carbon, nitrogen, silicon, and the halides.

Americium is a ductile, malleable metal which is precipitated by the fluorides, hydroxides, and oxalates. The element exists in three oxidation states in aqueous solution. The trivalent state is highly stable and difficult to oxidize. Curium is chemically similar to gadolenium and is carried on rare-earth precipitates. The only stable oxidation state that has been definitely identified in aqueous solutions is +3.

2. RADIATION HAZARD

Plutonium is one of the most dangerous posions known. The permissible levels of concentration of plutonium in air and water are the lowest of any of the radioactive elements. This is a result of the concentration of plutonium directly in the blood-forming sections of the bone, rather than the more uniform bone distribution shown by other heavy elements. Americium and curium are also extremely hazardous radioactive materials.

The effects of their radiation exposure are primarily dependent on the amount of radiation and the portion of the body affected. The effects of acute whole-body radiation exposure are: (1) 0 to 25 rem, no detectable clinical effects; (2) 25 to 200 rem, delayed effects and possible shortened life expectancy of 1 percent; (3) 200 to 600 rem, possible premature death; (4) greater than 600 rem, death. These effects are for a single large dose of radiation or a series of substantial doses in a short interval of time to the total body. The dose delivered to a particular body organ following the inhalation of 1 microcurie of each of these radionuclides is attached (Table 4). For plutonium-239 the dose delivered to the bone is 7,000 rem following the inhalation of 1 microcurie (16.4 micrograms). The dose delivered to the bone following the injection of 1 microcurie into the body via a wound is 30,000 rem.

Standards for prolonged exposure over a fifty year period have defined the single dose limit in terms of the maximum permissible dose accumulated in a period of 13 weeks. The whole body exposure limit is 3 rem per quarter and the accumulated dose limit is 5(N - 18), where N is the individual's age in years. Limits for the thyroid, bone, and other organs have also been defined. Values of the total body burden for each radionuclide required to produce the maximum permissible dose rates defined above have been compiled.[0563] For plutonium the critical organ is the bone and the maximum permissible body burden is 0.04 microcuries for Pu-238, Pu-239, and Pu-240 and 0.9 microcuries for Pu-241. For americium-241 and americium-243 the critical organ is the bone and the maximum permissible body burden is 0.05 microcuries. For curium-242 the critical organ is the liver and the maximum body burden is 0.05 microcuries. For curium-244 the critical organ is the bone and the maximum body burden is 0.1 microcuries.

3. OTHER HAZARDS

Besides its radiation hazard, plutonium is highly toxic. It is also highly reactive in moist air. The toxicity of curium and americium are unknown.[0766] Plutonium, americium, and curium also present a potential hazard due to nuclear fission. Plutonium-239 represents the greatest hazard since it readily undergoes fission with thermal neutrons, as well as with those of higher energy and is capable of maintaining a self-sustaining reaction.

4. DEFINITION OF ADEQUATE MANAGEMENT

These radionuclides are estremely hazardous because of their radiotoxicity. Semi-remote handling techniques are required to protect personnel from radiation injury and adequate radiation shielding is required to avoid excessive radiation exposure. These radionuclides are all alpha emitters except for plutonium-241. The alpha particles have little penetrating power and can be stopped by a sheet of writing paper. These materials are safely handled in glove boxes. The beta particles emitted by plutonium-241 are of low energy (0.021 Mev) and cannot penetrate more than 0.002 in. of water.

These radionuclides should be stored in controlled reservations in specially constructed containers or storage bins. Extreme precautions should be taken to avoid the release of any material. Plutonium should be stored at low temperatures and in dry air to avoid corrosion. The storage container should be protected by both a primary and a secondary containment barrier. Precautions must also be taken to prevent the formation of a critical mass. Plutonium in a liquid solution is more likely to become critical than solid plutonium. The container design and arrangement must preclude any possibility of obtaining nuclear criticality. Special monitoring systems and proper warning signs should be located in the general area of the storage facility.

Plutonium, americium, and curium are classified as a transport group I radionuclide by the Department of Transportation, and the rules and regulations governing their transportation are given in the Code of Federal Regulations (CFR) Title 49--Transportation, Parts 170 to 190.[2150] Their content is limited to 0.001 curies for a Type A package and 20 curies for a Type B package defined in 49CFR173. The limits are increased to 20 and 500 curies if their physical form meets the requirements of a special form material. Their release rate is limited to zero under the specified accident conditions for Type A and B quantities.[2150] Plutonium-239 is designated as a fissile material by the Department of Transportation and must meet the controls required to provide nuclear criticality safety.

Disposal/Reuse

The disposal of these materials is governed by the AEC Manual Chapter 0524 [0559] and 10CFR20. [2149] Two sets of standards have been established for the permissible radiation exposure in unrestricted areas. One is for the greatest dose received by an individual and the other for the average dose received by the general population. The standards for the safe release of these materials to the environment in an unrestricted area are contained in 10CFR20 [2149] and their release should not exceed the concentrations in air and water listed in this report (Table 5). These release rates apply to an individual and their release may be limited if a suitable sample of the population is exposed to one-third the concentrations in air or water specified in this report (Table 5).

The disposal by release in a sanitary sewage system is limited to 0.1 microcurie. [2149] The disposal by burial at any one location and time is limited to 10 microcuries. [2149]

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Recovery

Option #1 - Solvent Extraction. Solvent extraction processes have successfully been used for well over a decade as the standard method for the recovery of up to 99.8 percent of the plutonium and uranium in spent reactor fuel elements. The basis for separation in this process is the differences in solubility of these materials in the organic and aqueous phase. Nearly all major fuel reprocessing facilities use the Purex solvent extraction process. These facilities include those operated under contract to the Atomic Energy Commission (AEC) and Nuclear Fuel Services facility at West Valley, New York, which is privately owned and operated. In the Purex process, the spent fuel elements are dissolved in nitric acid and an organic compound, tributyl phosphate (TBP) in an inert hydrocarbon, is added. When this organic mixture is added, the TBP extracts both the uranium and the plutonium into the organic phase, while the fission products and other wastes remain in the aqueous phase. Plutonium and uranium are separated by reducing the plutonium to the trivalent form, usually with ferrous sulfamate, and contacting with nitric acid. In the aquafluor process, to be used at General Electric's Morris, Illinois plant, the uranium and plutonium separation will be accomplished by ion exchange. The ion exchange separation step will limit the plants capacity since they must be designed to prevent the accumulation of a critical mass.

Disposal

Option #1 - Land Burial. Disposal of these radionuclides, in small concentrations, by direct burial in unlined trenches is not considered a satisfactory means of disposal. These types of wastes are presently disposed of in this manner at approved sites. This method of disposal does not provide for any type of secondary containment barrier to prevent their release by leaching with the local ground water. Since these materials have an extremely long half-life and a high radiotoxicity this method of disposal is not satisfactory.

Option #2 - Near-Surface Liquid Storage. Near-surface storage of these radionuclides in stainless steel tanks encased in concrete and buried underground is not considered as a satisfactory means of disposal. Liquid reactor wastes have been stored in this manner over the past 25 years. At the present time these tanks are considered as an interim storage technique due to a general lack of confidence in their long-term integrity.[0705] Therefore, the near-surface storage of these wastes in steel tanks should only be considered as a near-term storage technique and not as a permanent storage or disposal technique.

Option #3 - Near-Surface Solid Storage. The disposal of solidified wastes in engineered surface facilities offers the best immediate method for disposal of these wastes. The technology for these facilities has been developed and the wastes will be under constant surveillance and control and can be retrieved, should this be required. The wastes should be solidified and encapsulated in a suitable container (stainless steel). Of the four high-level solidification processes developed for reactor-produced wastes, spray solidification offers the best solidified waste characteristics (see Radioactive Waste Solidification report). The wastes will be stored in stainless steel vaults encased in concrete. The vaults will be either air or water cooled. The periodic replacement of the waste containers will be required due to the extremely long half-life of these elements.

Option #4 - Salt Deposits. This method offers the greatest potential for the disposal of plutonium, americium, and curium wastes since bedded salt deposits are completely free of circulating ground waters. This method of disposal has been under study by the Oak Ridge National Laboratory since 1957, and in November of 1970 a committee of the National Academy of Sciences recommended that the use of bedded salt for the disposal of radioactive wastes is satisfactory.[0733] The wastes must be solidified and disposed of in the solid form encapsulated in a suitable container. The solidified wastes are then buried in rooms carved in the salt deposits approximately 1,000 feet below the ground. The salt is a good heat transmitter, provides about the same radioactive shielding as concrete, and can heal its own fractures by plastic flow. The critical problem is the selection of a site that meets the necessary design and geological criteria. For these wastes the life of the mine must extend beyond several thousand years. Salt deposits should be considered for the disposal of these wastes at approved sites that are acceptable from a design and geological standpoint. In addition, a method of waste retrieval is required in the event the integrity of the site is destroyed.

Option #5 - Bedrock Disposal. The disposal of liquid wastes along with other spent reactor wastes in vaults excavated in crystalline rock over 1,500 ft beneath the ground is currently being evaluated by E. I. Du Pont de Nemours, at their Savannah River Plant near Aiken, South Carolina.[0894, 1396] An advisory committee appointed by the

National Academy of Sciences recommended abandonment of the project. In May 1972, another National Academy of Sciences panel concluded that bedrock storage provides a reasonable prospect for long-term safe storage, but an unprecedented degree of precise information is needed to decide if and where underground storage vaults should be built. Another method has also been proposed for disposing of liquid wastes by in situ incorporation in molten silicate rock.[2146] At the present time both of these methods are unsatisfactory since sufficient engineering data or exploration has not been completed to verify their suitability. Due to the long half-life and high biological hazard of the transuranium elements, it is doubtful that data could ever be accumulated to prove that the geological characteristics of the site over the next few thousand years are acceptable to ensure the absolute safety of such a disposal method.

To summarize, plutonium, americium, and curium are extremely hazardous long-lived isotopes for which extreme precautions are required in their disposal. Plutonium is separated from the reactor-produced wastes by solvent extraction for reuse. Recovery factors as high as 99.8 percent can be obtained. The americium, curium, and remaining plutonium are contained with the other reactor wastes. The acceptable method of treatment is spray solidification and disposal in either salt deposits or near-surface engineered facilities. Plutonium, americium, and curium wastes from research laboratories and other sources should also be solidified, encapsulated, and disposed of in the same manner.

6. APPLICABILITY TO NATIONAL DISPOSAL SITE

Plutonium, americium, and curium are candidates for a National Disposal Site due to their long half-life, extreme health hazard, and projected growth with that of the civilian nuclear power program. The recommended processes for the disposal of these radionuclides are:

Process	Order of Preference	Remarks
Near-surface solid storage	First choice	Demonstrated technology; waste under constant surveillance and control and can be retrieved.
Salt beds	Second choice	Affords permanent disposal without constant surveillance; further development required for a waste retrieval plan and location of an acceptable site.

For each of these processes the wastes should be solidified and encapsulated in a suitable container.

7. REFERENCES

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HAZARDOUS WASTES PROPERTIES WORKSHEET

Name Plutonium-238

Half-life 86.4 years

Type of Decay Alpha and Spontaneous Fission

Structural Formula

$_{94}Pu^{238}$

Molecular Wt. 238 Melting Pt. 639 C Boiling Pt. 3235 C

Density 19.84 gm/cc Specific Power 0.56 watts/gm

Specific Activity 17.4 curries/gm

Solubility

Cold Water Hot Water

Others: Soluble HCl; insoluble in HNO_3 and concentrated H_2SO_4

Decay Chain

$$_{94}Pu^{238} \xrightarrow{\alpha} {}_{92}U^{234}$$

(86.4y) ($2.5X10^5$y)

Radiation Energy Level & Intensities

Alpha: 5.499 Mev (72%)
5.456 Mev (28%)

Gamma: 0.0435 Mev (0.04%)

Shipping Regulations Classified as a transport group I radionuclide by the Department of Transportation

Comments

References: (1) 0766
(2) 2147
(3) 2150

HAZARDOUS WASTES PROPERTIES WORKSHEET

Name Plutonium-239

Half-life 24,400 years

Type of Decay Alpha and Spontaneous Fission

Structural Formula

$_{94}Pu^{239}$

Molecular Wt. 239 Melting Pt. 639 C Boiling Pt. 3235 C

Density 19.84 gm/cc Specific Power 0.0019 watts/gm

Specific Activity 0.061 curries/gm

Solubility

Cold Water Hot Water

Others: Soluble HCl, insoluble in HNO_3 and concentrated H_2SO_4

Decay Chain

$$\underset{(2.4\times10^4 y)}{_{94}Pu^{239}} \xrightarrow{\alpha} \underset{(7.1\times10^8 y)}{_{92}U^{235}}$$

Radiation Energy Level & Intensities

Alpha: 5.157 Mev (74%)
5.145 Mev (15%)
5.107 Mev (11%)

Gamma: 0.414 Mev (0.0001%)
0.375 Mev (0.0001%)
0.129 Mev (0.005%)
0.052 Mev (0.020%)
0.039 Mev (0.007%)

Shipping Regulations

Comments Classified as a transport group I radionuclide by the Department of Transportation

References: (1) 0766
(2) 2147
(3) 2150

HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Plutonium-240

Half-life 6,580 years

Type of Decay Alpha and Spontaneous Fission

Structural Formula

$_{94}Pu^{240}$

Molecular Wt. 240

Melting Pt. 639 C

Boiling Pt. 3235 C

Density 19.84 gm/cc

Specific Power 0.0069 watts/gm

Specific Activity 0.227 curries/gm

Solubility

Cold Water

Hot Water

Others: soluble HCl; insoluble in HNO_3 and concentrated H_2SO_4

Decay Chain

$$\begin{array}{ccc} {}_{94}Pu^{240} & \xrightarrow{\alpha} & {}_{92}U^{236} \\ (6580y) & & (2.4\times10^{7}y) \end{array}$$

Radiation Energy Level & Intensities

Alpha: 5.168 Mev (76%)
5.123 Mev (29%)

Gamma: 0.045 Mev (24%)

Shipping Regulations Classified as a transport group I radionuclide by the Department of Transportation

Comments

References: (1) 0766
(2) 2147
(3) 2150

HAZARDOUS WASTES PROPERTIES WORKSHEET

Name Plutonium-241

Structural Formula $_{94}Pu^{241}$

Half-life 13.2 years

Type of Decay Negative Beta

Molecular Wt. 241

Melting Pt. 639 C

Boiling Pt. 3235 C

Density 19.84 gm/cc

Specific Power 0.0048 watts/gm

Specific Activity 112 curries/gm

Solubility

Cold Water

Hot Water

Others: Soluble HCl; insoluble in HNO_3 and concentrated H_2SO_4

Decay Chain

$$_{94}Pu^{241} \xrightarrow{\beta^-} {}_{95}Am^{241}$$

(13.2y) (458y)

Radiation Energy Level & Intensities

Beta: 0.021 Mev (100%)

Also emits alpha particle 0.0023% of the time.

Shipping Regulations Classified as a transport group I radionuclide by the Department of Transportation.

Comments

References: (1) 0766
(2) 2147
(3) 2150

HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Americium-241

Half-life 458 years

Type of Decay Alpha and Spontaneous Fission

Structural Formula

$_{95}Am^{241}$

Molecular Wt. 241 Melting Pt. 994 C Boiling Pt. 2607 C

Density 11.7 gm/cc

Specific Power 0.11 watts/gm

Specific Activity 3.24 curries/gm

Solubility

Cold Water

Hot Water

Others: Soluble in dilute acid

Decay Chain

$$\underset{(458y)}{_{95}Am^{241}} \xrightarrow{\alpha} \underset{(2X10^6y)}{_{93}Np^{237}}$$

Radiation Energy Level & Intensities

Alpha: 5.486 Mev (86%)
5.443 Mev (12.7%)
5.389 Mev (1.3%)

Gamma: 0.060 Mev (36%)
0.026 Mev (3%)

Shipping Regulations Classified as a transport group I radionuclide by the Department of Transportation.

Comments

References: (1) 0766
(2) 2150
(3)

HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Americium-243

Half-life 7,950 years

Type of Decay Alpha

Molecular Wt. 243

Melting Pt. 994 C

Boiling Pt. 2607 C

Density 11.7 gm/cc

Specific Power 0.0062 watts/gm

Specific Activity 0.185 curries/gm

Structural Formula

$${}_{95}Am^{243}$$

Solubility

Cold Water

Hot Water

Others: Soluble in dilute acid

Decay Chain

$${}_{95}Am^{243} \xrightarrow{\alpha} {}_{93}Np^{239} \xrightarrow{B^-} {}_{94}Pu^{239}$$

(7,950y) (2.4d) $(2.4X10^4y)$

Radiation Energy Level & Intensities

Americium-243

Alpha: 5.276 Mev (88%)
5.234 Mev (11%)
5.181 Mev (1.1%)

Gamma: 0.075 Mev (50%)
0.044 Mev (4%)

Neptunium-239

Beta: 0.437 Mev (Max)

Shipping Regulations Classified as a transport group I radionuclide by the Department of Transportation.

Comments

References: (1) 0766
(2) 2150
(3)

HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Curium-242

Half-life 163 days

Type of Decay Alpha and Spontaneous Fission

Structural Formula

$_{96}Cm^{242}$

Molecular Wt. 242 Melting Pt. 1340 C Boiling Pt. ______

Density 7 gm/cc

Specific Power 122 watts/gm

Specific Activity 3,320 curries/gm

Solubility

Cold Water ______ Hot Water ______

Others: ______

Decay Chain

$$_{96}Cm^{242} \xrightarrow{\alpha} {}_{94}Pu^{238}$$

(163d) (86 years)

Radiation Energy Level & Intensities

Alpha: 6.115 Mev (74%)
6.071 Mev (26%)

Gamma: 0.158 Mev (.003%)
0.102 Mev (.004%)
0.044 Mev (.041%)

Shipping Regulations Classified as a transport group I radionuclide by the Department of Transportation.

Comments ______

References: (1) 0766
(2) 2147
(3) 2150

HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Curium-244

Half-life 17.6 years

Type of Decay Alpha and Spontaneous Fission

Structural Formula

$_{96}\text{Cm}^{244}$

Molecular Wt. 244 Melting Pt. 1340 C Boiling Pt.

Density 7 gm/cc Specific Power 2.7 watts/gm

Specific Activity 83 curries/gm

Solubility

Cold Water Hot Water

Others:

Decay Chain

$$_{96}\text{Cm}^{244} \xrightarrow{\alpha} {}_{92}\text{Pu}^{240}$$

(17.6y) (6580y)

Radiation Energy Level & Intensities

Alpha: 5.806 Mev (77%)
5.766 Mev (23%)

Gamma: 0.150 Mev (.0013%)
0.100 Mev (.0015%)
0.043 Mev (.0210%)

Shipping Regulations Classified as a transport group I radionuclide by the Department of Transportation.

Comments

References: (1) 0766
(2) 2147
(3) 2156

TABLE 1

AMERICIUM-243 DECAY CHAIN

NUCLIDE	NAME	HALF-LIFE	MAJOR RADIATION
$_{95}\mathrm{Am}^{243}$	Americium-243	7,950 years	Alpha and gamma
$_{93}\mathrm{Np}^{239}$	Neptunium-239	2.4 days	Beta and gamma
$_{94}\mathrm{Pu}^{239}$	Plutonium-239	24,400 years	Alpha and gamma
$_{92}\mathrm{U}^{235}$	Uranium-235	7.1×10^{8} years	Alpha and gamma
$_{90}\mathrm{Th}^{231}$	Thorium-231	25 hours	Beta and gamma
$_{91}\mathrm{Pa}^{231}$	Protactinium-231	3.3×10^{4} years	Alpha and gamma
$_{89}\mathrm{Ac}^{227}$	Actinium-227	21.6 years	Beta and gamma
$_{90}\mathrm{Th}^{227}$	Thorium-227	18.2 days	Alpha and gamma
$_{88}\mathrm{Ra}^{223}$	Radium-223	11.4 days	Alpha and gamma
$_{86}\mathrm{Rn}^{219}$	Radon-219	4 seconds	Alpha and gamma
$_{84}\mathrm{Po}^{215}$	Polonium-215	1.8 minutes	Alpha
$_{82}\mathrm{Pb}^{211}$	Lead-211	36 minutes	Beta and gamma
$_{83}\mathrm{Bi}^{211}$	Bismuth-211	2 minutes	Alpha, beta, and gamma
$_{81}\mathrm{Tl}^{207}$	Thallium-207	4.8 minutes	Beta and gamma
$_{82}\mathrm{Pb}^{207}$	Lead-207	Stable	

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TABLE 2
ACCUMULATED WASTES FROM THE CIVILIAN NUCLEAR POWER PROGRAM [0705]

Accumulated Radionuclides megacuries	Calendar Year 1970	1980	1990	2000	2020
Plutonium-238*	0.002	1.2	8.3	30.7	166
Plutonium-239*	0.00009	0.02	0.24	1.3	8.5
Plutonium-240*	0.0001	0.04	0.4	1.9	11.4
Plutonium-241*	0.03	6.6	47.2	191	909
Americium-241	0.009	2.3	22.7	121	763
Americium-243	0.0009	0.23	1.5	5.2	27.0
Curium-242	0.73	43.2	185	487	1,490
Curium-244	0.13	29.9	137	255	700

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*Assumes that 0.5 percent of the plutonium in the spent fuel is lost to waste.

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TABLE 3

ACTIVITY OF PLUTONIUM, AMERICIUM, AND CURIUM PRODUCTS PRESENT IN WASTES GENERATED BY THE PROCESSING OF SPENT REACTOR FUELS[0705]+

Light Water Reactor Fuels
(Fuel Exposed to 33 MWD/Tonne* at 30 MW/Tonne)

Actinide Products	After 1 year Grams/Tonne	After 1 year Watts/Tonne	After 1 year Curies/Tonne	After 100 years Grams/Tonne	After 100 years Watts/Tonne	After 100 years Curies/Tonne
Pu^{238}, Pu^{239}, Pu^{240}, Pu^{241}	48	2.7	641	71	2	64
Am^{241}, Am^{243}	144	6.2	189	140	6	179
Cm^{242}, Cm^{244}	32	306	8,430	1	2	57
Other Actinides	5,436	0.1	30	5,438	0.1	25

Fast-Breeder Reactor Fuels
(Fuel Exposed to 33 MWD/Tonne at 58 MW/Tonne)

Actinide Products	After 1 year Grams/Tonne	After 1 year Watts/Tonne	After 1 year Curies/Tonne	After 100 years Grams/Tonne	After 100 years Watts/Tonne	After 100 years Curies/Tonne
Pu^{238}, Pu^{239}, Pu^{240}, Pu^{241}	428	11	3,203	412	8	264
Am^{241}, Am^{243}	742	54	1,620	794	48	1,469
Cm^{242}, Cm^{244}	20	625	17,000	1	3	72
Other Actinides	4,550	2	277	4,637	1	165

*Tonne is a metric ton of reactor fuel.

+Assumes that 0.5 percent of the plutonium in the spent fuel is lost to waste.

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TABLE 4

PLUTONIUM, AMERICIUM, AND CURIUM DOSE TO A PARTICULAR BODY ORGAN FOLLOWING INHALATION OF ONE MICROCURIE OF THE NUCLIDE

Isotope	Form	Organ	Dose rem
Plutonium-238	Insoluble	Lung	64
Plutonium-238	Soluble	Bone	700
Plutonium-239	Insoluble	Lung	60
Plutonium-239	Soluble	Bone	7,000
Plutonium-240	Insoluble	Lung	60
Plutonium-240	Soluble	Bone	7,000
Plutonium-241	Insoluble	Lung	0.06
Plutonium-241	Soluble	Bone	130
Americium-241	Insoluble	Lung	65
Americium-241	Soluble	Bone	2,200
Americium-243	Insoluble	Lung	60
Americium-243	Soluble	Bone	2,000
Curium-242	Insoluble	Lung	43
Curium-242	Soluble	Liver	50
Curium-244	Insoluble	Lung	67
Curium-244	Soluble	Bone	1,300

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TABLE 5

PLUTONIUM, AMERICIUM, AND CURIUM ENVIRONMENTAL RELEASE RATES [2149]

Radionuclide	Form	Concentration in Air (microcuries/milliliter)	Concentration in Water (microcuries/milliliter)
Plutonium-238	Soluble	7×10^{-14}	5×10^{-6}
Plutonium-238	Insoluble	1×10^{-12}	3×10^{-5}
Plutonium-239	Soluble	6×10^{-14}	5×10^{-6}
Plutonium-239	Insoluble	1×10^{-12}	3×10^{-5}
Plutonium-240	Soluble	6×10^{-14}	5×10^{-6}
Plutonium-240	Insoluble	1×10^{-12}	3×10^{-5}
Plutonium-241	Soluble	3×10^{-12}	2×10^{-4}
Plutonium-241	Insoluble	1×10^{-9}	1×10^{-3}
Americium-241	Soluble	2×10^{-13}	4×10^{-6}
Americium-241	Insoluble	4×10^{-12}	2×10^{-5}
Americium-243	Soluble	2×10^{-13}	4×10^{-6}
Americium-243	Insoluble	4×10^{-12}	3×10^{-5}
Curium-242	Soluble	4×10^{-12}	2×10^{-5}
Curium-242	Insoluble	6×10^{-12}	3×10^{-5}
Curium-244	Soluble	3×10^{-13}	7×10^{-6}
Curium-244	Insoluble	3×10^{-12}	3×10^{-5}

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PROFILE REPORT

Ruthenium-106 (Rhodium-106), Cerium-144 (Praseodymium-144), Promethium-147

I. GENERAL

Introduction

Ruthenium-106, cerium-144, and promethium-147 are radioactive isotopes that are produced in nuclear reactors by the fission of uranium. Ruthenium-106 has a half-life of 368 days and emits only beta particles. It exists in radiation equilibrium with its short half-lived daughter, rhodium-106. Rhodium-106 has a half-life of 30 seconds and emits both gamma rays and high energy (3.55 Mev) beta particles. Cerium-144 is both a beta and gamma emitter and has a half-life of 284 days. It decays by beta emission to form praseodymium-144 which has a half-life of 17.3 minutes. Promethium-147 has a half-life of 2.62 years and decays by the emission of a 0.224 beta particle to form stable samarium-147.

These three isotopes, Ru-106, Ce-144, and Pm-147, have a moderately long half-life (284 days to 2.6 years) and together with their short half-lived daughters account for a majority of the total fission product activity and heat content in the wastes generated at nuclear power plants. After one year of radioactive decay, they are responsible for 65 percent of the total heat content and for 70 percent of the total activity.

Since these isotopes are principally produced in nuclear reactors, their projected growth will parallel that of the civilian nuclear power program. Present projections indicate that the total installed capacity of nuclear power plants will grow by a factor of 60 between 1970 and 1985.[2148] Annual production figures from the civilian and nuclear power program for these three radionuclides to the year 2020 for light-water and fast-breeder reactor fuels are attached (Table 1 to 3). These figures illustrate the tremendous growth anticipated in their production.

Manufacture

Presently, these three radionuclides are produced in thermal reactors by the fission of uranium. The fission yield for these three radionuclides is: cerium-144, 5.6 percent; promethium-147, 2.6 percent; and ruthenium-106, 0.38 percent. Civilian nuclear power plants are the major producers and a smaller amount is produced at AEC facilities. At the present time there are 22 nuclear power plants in operation with an additional 104 being built or planned.[2151] In the future they will also be produced in fast-breeder reactors by the fission of plutonium.

Uses

Promethium-147 is used in radioisotope power generators and as a beta source in the radioactive gauge field. It is also used in the preparation of self-illuminating materials and devices for signs and signals. At the present time promethium-147 is separated from the reactor-produced waste streams and distributed by the AEC through the Oak Ridge National Laboratory, Isotope Sales Department. The AEC revenue from its distribution for the years 1968 to 1971 is[2151]:

Year	Revenue (Dollars)
1968	56,000
1969	45,000
1970	16,000
1971	30,000

In the future when its production is warranted by market demands, it would be available in large quantities from commercial firms operating chemical reprocessing plants. The commercial use for ruthenium-106 and cerium-144 is very limited.

Sources and Types of Wastes

Ruthenium-106, cerium-144. and promethium-147 are produced in nuclear reactors and are contained within the spent fuel elements. The spent fuel elements are removed from the reactor and processed for the recovery of usable fissionable materials. These radionuclides and the other high-level wastes are contained in the aqueous effluent from the reprocessing step. The range of chemical compositions of these waste streams have been tabulated.[0715] These waste streams are primarily aqueous solutions of inorganic nitrate salts and any differences in their composition occurs mainly in the amounts and types of salts added during the reprocessing step. The amount and activity of Ru-106, Ce-144, and Pm-147 present in the spent reactor waste streams after one year and ten years is attached (Table 4).

These radionuclides can also be found in the secondary waste streams generated at the fuel reprocessing plant. The volume of these waste streams can be quite large but the radionuclide activity in these streams is quite low. Ruthenium-106 which will usually oxidize and volatilize during the fuel reprocessing step is also found in the off-gas streams.

Physical and Chemical Properties

The physical and chemical properties of ruthenium-106, cerium-144, and promethium-147 are included in the attached worksheets. Ruthenium-106 exhibits all possible positive valences; consequently, its chemistry is exceedingly complex. In the lower oxidation states it is basic in nature, while in the higher oxidation states it tends to be acidic. In alkaline solutions it may be oxidized to the ruthenite, ruthenate, perruthenate, or the tetroxide, depending upon the strength of the oxidizing agent. The tetroxide is volatile, boiling at around [illegible].

Cerium-144 is a member of the rare-earth group. Cerium has a valence of +3 but can also assume a valence of +4. Tetravalent cerium is a powerful oxidizing agent. The hydroxides and [illegible] of cerium are slightly soluble in water. The carbonates, oxalates, and [illegible] are not soluble. Promethium-147 is also a member of the rare-earth group and its chemistry is similar to that of cerium.

2. RADIATION HAZARD

Ruthenium-106 and cerium-144 are dangerous radioactive materials. Promethium-147 is a moderately dangerous radioactive material. The effects of their radiation exposure are primarily dependent on the amount of radiation and the portion of the body affected. The effects of acute whole-body radiation exposure are: (1) 0 to 25 rem, no detectable clinical effects; (2) 25 to 200 rem, delayed effects and possible shortened life expectancy of 1 percent; (3) 200 to 600 rem, possible premature death; (4) greater than 600 rem, death. These effects are for a single large dose of radiation or a series of substantial doses in a short interval of time to the total body. Standards for prolonged exposure over a fifty-year period have defined the single dose limit in terms of the maximum permissible dose accumulated in a period of 13 weeks. The whole body exposure limit is 3 rem per quarter and the accumulated dose limit is 5(N - 18), where N is the individual's age in years. Limits for the thyroid, bone, and other organs have also been defined.[0563]

Values of the total body burden for each radionuclide required to produce the maximum permissible dose rates defined above have been compiled.[0563] For ruthenium-106 the critical organ is the kidney and the maximum permissible body burden is 3 microcuries. For cerium-144 and promethium-147 the critical organ is the bone and the maximum permissible body burden is 5 microcuries and 60 microcuries, respectively

Their radiological toxicity can also be expressed in terms of the dose delivered to a particular body organ following the inhalation of 1 microcurie. For each of these radionuclides the single inhalation of 1 microcurie will produce the following doses:

Isotope	Form	Organ	Dose
Ru-106	Insoluble	Lung	1.2 rem
Ru-106	Soluble	Kidney	0.04 rem
Ce-144	Insoluble	Lung	1.0 rem
Ce-144	Soluble	Bone	1.1 rem
Pm-147	Insoluble	Lung	0.07 rem
Pm-147	Soluble	Bone	0.2 rem

3. OTHER HAZARDS

Cerium-144 resembles aluminum in its pharmacological action as well as in its chemical properties. Besides its radiation hazard, cerium-144 is not toxic to the skin or mucous membranes by repeated exposure and is only slightly toxic if absorbed into the body by inhalation or injection.[0766] Its fire and explosive hazard is moderate. It does ignite spontaneously in air at temperatures of 150 C to 180 C. The toxicity of cerium compounds is the same as cerium, except when the anion has a toxicity of its own.

The details of ruthenium-106 toxicity are unknown, but is believed to be toxic.[0776] It is dangerous when heated to decomposition since it emits toxic fumes of ruthenium oxide. Data on the toxicity of promethium-147 were not available.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Since all three radionuclides are hazardous to man by inhalation, ingestion,or direct radiation exposure, great care must be exercised in their handling. Handling must be set up to prevent excessive exposure to personnel and in fact to prevent any unnecessary exposure. Special procedures and adequate radiation shielding are required in their handling. The beta particles emitted by Ru-106, Ce-144, and Pm-147 are of low energy and cannot penetrate more than 0.02 in. of water. The daughter products of Ru-106 and Ce-144 do emit high energy beta particles which can penetrate up to 0.8 in. of water. The principal shielding problem associated with their daughter's beta radiation is the bremsstrahlung effect which results from the presence of highly penetrating rays resulting from the deflection of the beta particles by the nuclei in the shielding medium. Since the bremsstrahlung effect increases with atomic number, shielding materials of high atomic weight are not satisfactory. Ru-106, Ce-144, and their daughters also emit gamma radiation. The gamma radiation is highly penetrating and high-density shields, such as lead, are required to stop the radiation. To detect and control personnel exposure to their radiation all persons working with this material should wear an external dosimetry device. The commonly used devices are the film badge and the thermoluminescent dosimeters (TLD).

These materials should be stored in controlled reservations in specially constructed containers or storage bins. They should be protected by both a primary and a secondary containment barrier. Special monitoring systems and proper warning signs should be located in the general area of the storage facility.

Ruthenium-106 and cerium-144 are classified as a transport group III radionuclide and promethium-147 as a transport group IV radionuclide by the Department of Transportation. The rules and regulations governing their transportation are given in the Code of Federal Regulations (CFR) Title 49--Transportation, Parts 170 to 190.[2150] The Ru-106 and Ce-144 content is limited to 3 curies for a Type A package and 200 curies for a Type B package defined in 49CFR173. The Pm-147 content is limited to 20 curies for a Type A package and 200 curies for a Type B package. These limits for each radionuclide are increased to 20 and 5,000 curies if their physical form meets the requirements of a special form material. Their release rate is limited to zero under the specified accident conditions for Type A and B quantities.[2150] The allowable release of radioactivity from packages containing large quantities of these materials is limited to gases and contaminated coolant containing total radioactivity exceeding neither

0.1 percent of the total radioactivity of the package nor 10 curies under the hypothetical accident conditions prescribed in 49CFR173.

Disposal/Reuse

The disposal of these materials is governed by the AEC Manual Chapter 0524 [0559] and 10CFR20. [2149] Two sets of standards have been established for the permissible radiation exposure in unrestricted areas. One is for the greatest dose received by an individual and the other for the average dose received by the general population. The radiation protection standards for these two groups are attached (Table 5). The standards for the safe disposal of these materials also define their maximum concentrations in air and water for exposure to either an individual or to the general population. For an individual, the safe release of these materials to the environment in an unrestricted area should not exceed the concentration in microcuries per milliliter (uc/ml) listed below [2149]:

Isotope	Form	Concentration in Air	Concentration in Water
Ru-106	Soluble	$3x10^{-9}$ uc/ml	$1x10^{-5}$ uc/ml
Ru-106	Insoluble	$2x10^{-10}$uc/ml	$1x10^{-5}$ uc/ml
Ce-144	Soluble	$3x10^{-10}$ uc/ml	$1x10^{-5}$ uc/ml
Ce-144	Insoluble	$2x10^{-10}$ uc/ml	$1x10^{-5}$ uc/ml
Rm-147	Soluble	$2x10^{-9}$ uc/ml	$2x10^{-4}$ uc/ml
Rm-147	Insoluble	$3x10^{-9}$ uc/ml	$2x10^{-4}$ uc/ml

The concentrations for the safe release of these materials to the general population are one-third the above values.

The disposal by release into a sanitary sewage system is limited to 10 microcuries for Ru-106 and Ce-144 and to 100 microcuries for Pm-147. The disposal by burial in the soil at any one location and time is limited to 1,000 microcuries for Ru-106 and Ce-144 and to 10,000 microcuries for Pm-147. [2149]

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Recovery

Option No. 1 - Volatilization-Absorption. Ruthenium-106 removal from solutions can be accomplished by oxidizing the ruthenium to its tetroxide state and volatilizing it by simultaneous heating and gas sparging. In the tetroxide state, ruthenium boils at 100 C. Ruthenium can be removed from uranium nitrate solutions by sparging with air containing ozone. Ruthenium decontamination factors (ratio of initial to final concentration) of about 100 were obtained during an 8-hour sparge with 1 percent ozone in air.[0714] Ruthenium can also be oxidized to the volatile form by hot concentrated nitric acid. The volatized ruthenium is then recovered by absorption. Two such absorbents are pyrolusite and activated carbon. Decontamination factors with pyrolusite alone are less than 100.[0714] Activated carbon used subsequent to pyrolusite absorption increases the decontamination factor 10 times.

Option No. 2 - Scavenging-Precipitation Foam Separation. The removal of radionuclides from low-level radioactive waste water by scavenging-precipitation form separation has been studied by Oak Ridge National Laboratory.[0703] The process consists of two steps: (1) precipitating in a sludge-blanket clarification step, and (2) achieving final decontamination in a foam-separation column. Processing rates of 300 gal per hour (gph) for scavenging-precipitation and 120 gph for foam separation have been achieved. Cerium-144 decontamination factors of greater than 20 have been obtained.[0703] Ruthenium-106 decontamination factors of only four were obtained. The low decontamination factor is expected since ruthenium is one of the most difficult radionuclides to remove by scavenging.

Option No. 3 - Scavenging-Precipitation Ion Exchange. In this process final decontamination is obtained by ion exchange columns from the scavenging-precipation process. The process includes a provision for the recycle of the ion exchange waste to the scavenging-precipitation step. All the removed radionuclides are concentrated in the clarifier sludge. For cerium-144 and promethium-147 the overall decontamination factors varied from 20 to 700 and for ruthenium-106 the overall decontamination factor varied from 1.5 to 8.[0705] For cerium-144 and promethium-147, the use of ion exchange resins with a scavenging-precipitation step is a fairly simple and efficient means of removing these radionuclides from low-level radioactive aqueous wastes. For ruthenium-106 wastes this method is not satisfactory since ruthenium in the liquid form is not very susceptible to ion exchange.

Option No. 4 - Water Recycle. The water recycle process is used for decontaminating radioactive waste water and recycling the purified water for reuse. This process has been demonstrated at the pilot plant scale by Oak Ridge National Laboratory.[0707] The steps in the process include: (1) clarification by controlled addition of coagulants, (2) demineralization by cation-anion exchange, and (3) sorption on granular activated carbon. For optimum removal of the ruthenium-106 during the coagulation-clarification step the pH of the waste must range between 7 and 8 for proper alum floc formation. High decontamination factors for ruthenium-106 can only be obtained during the final step by sorption on activated carbon. The overall decontamination factor for ruthenium-106 was 1,230 and for cerium-144 it was 800. The method is an improvement to the treat-and-discharge methods, but further work is required until full-scale production use is obtained.

Disposal

Option No. 1 - Land Burial. Land burial of Ru-106, Ce-144 and Pm-147 wastes, in small concentrations, at approved sites that are acceptable from a geologic and hydrologic standpoint, is an acceptable means of disposal. Their concentrations should not be in excess of 10^4 times the maximum permissible concentration for the general population in 10CFR20.[2149] All wastes to be disposed of should be in a solid form and encapsulated in a suitable container. Liquid wastes should be solidified, preferably using asphalt, in accordance with the methods described in the radioactive waste solidification report. The burial trenches should be designed not to intercept the ground water table and constructed with a bottom drain and sump for water monitoring. The trenches should be covered with either asphalt or vegetation to prevent infiltration of water. The burial site design, geology, and hydrology should be in conformance with the criteria used in selecting and licensing the present commercial burial sites.[1423] Since land burial has successfully been practiced on a commercial scale and these isotopes have moderate half-lives, it should be considered as the most satisfactory method of disposing of all dilute concentrations of these wastes.

Option No. 2 - Near-Surface Liquid Storage. Near-surface storage of reactor produced liquid wastes in stainless steel tanks encased in concrete and buried underground is not considered as a satisfactory means of disposal. Liquid reactor wastes have been stored in this manner over the past 25 years. The tanks range in size from 0.33 to 1.3 million gal and are generally equipped with devices for measuring temperatures, liquid levels, and leaks. At the present time these tanks are considered as an interim storage technique due to a general lack of confidence in their long-term integrity.[0705] In addition, present regulations require the solidification of all reactor wastes within five years following reprocessing.[2149] Therefore, the near-surface storage of these wastes in steel tanks should only be considered as a near-term storage technique and not as a permanent storage or disposal technique.

Option No. 3 - Near-Surface Solid Storage. The disposal of high-level solidified Ru-106, Ce-144 and Pm-147 wastes in engineered surface facilities offers the best immediate method for disposal of these wastes. The technology for these facilities has been developed and the wastes will be under surveillance and control and can be retrieved, should this be required. The reactor-produced wastes should be solidified and encapsulated in a suitable container (stainless steel). Of the four high-level solidification processes developed, spray solidification offers the best solidified waste characteristics (see Radioactive Waste Solidification report). The wastes will be stored in stainless steel vaults encased in concrete. The vaults will be either air or water cooled. The periodic replacement of the waste containers probably will not be required since their activity is reduced by a factor of 1,000 in 10 years for Ru-106 wastes, in 21 years for Ce-144 wastes, and in 26 years for Pm-147 wastes. The replacement of the wastes containers might be required if other long-lived isotopes are also present.

Option No. 4 - Salt Deposits. This method offers the greatest potential for the disposal of reactor-produced Ru-106, Ce-144, and Pm-147 wastes since bedded salt deposits are completely free of circulating ground waters. This method of disposal has been under study by the Oak Ridge National Laboratory since 1957, and in November of 1970 a committee of the National Academy of Sciences recommended that the use of bedded salt for the disposal of radioactive wastes is satisfactory. [0733] The reactor-produced wastes must be solidified and disposed of in the solid form encapsulated in a suitable container. The preferred solidification process is spray solidification. The solidified wastes are then buried in rooms carved in the salt deposits approximately 1,000 feet below the ground. The salt is a good heat transmitter, provides about the same radioactive shielding as concrete, and can heal its own fractures by plastic flow. Salt deposits should be considered for the disposal of these wastes at approved sites that are acceptable from a design and geological standpoint. In addition, a method of waste retrieval is required in the event the integrity of the site is destroyed.

Option No. 5 - Bedrock Disposal. The disposal of liquid wastes along with other spent reactor wastes in vaults excavated in crystalline rock over 1,500 feet beneath the ground is currently being evaluated by E. I. du Pont de Nemours, at their Savannah River Plant near Aiken, South Carolina. [0894, 1396] The wastes would be stored in six tunnels and once in the tunnels the wastes will seep into the surrounding rock. Located above the crystalline rock is the Tuscaloosa formation, a good source of freshwater, which is separated by a layer of clay that would act as a barrier to the leakage of radioactive wastes. An advisory committee appointed by the National Academy of Sciences recommended abandonment of the project. In May 1972, another National Academy of Sciences panel concluded that bedrock storage provides a reasonable prospect for long-term safe storage but an unprecedented degree of precise information is needed to decide if and where underground storage vaults should be built. Another method has also been proposed for disposing of liquid wastes by in situ incorporation in molten silicate rock.[2146] At the present time both of these methods are unsatisfactory since sufficient engineering data or exploration has not been completed to verify their suitability.

Option No. 6 - Hydraulic Fracturing. The direct disposal of aqueous intermediate-level radioactive wastes into shale formations has been investigated by Oak Ridge National Laboratory.[0709] The method consists of mining the aqueous wastes with cement and pumping the resulting slurry down a well out into a nearly horizontal fracture in a thick shale formation. Since no additional encapsulation is provided, this method of disposal is not satisfactory.

To summarize, ruthenium-106, cerium-144, and promethium-147 are radioactive isotopes that account for a majority of the initial activity present in reactor-produced wastes. The acceptable method of treatment is solidification and disposal in near-surface engineered facilities or salt deposits. Cerium-144 and promethium-147 can be recovered from low-level liquid waste streams by scavenging-precipitation ion exchange. Ruthenium-106 can be recovered by volatization and absorption on pyrolusite and activated carbon. Generally, during the reprocessing of uranium and plutonium it is desirable to prevent the volatization of ruthenium. This can be accomplished during the leaching operation by adding a reducing agent such as sodium nitrite or nitrogen dioxide to suppress the ruthenium volatilization.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Ruthenium-106, cerium-144, and promethium-147 are candidates for a National Disposal Site. The applicability of the recovery processes to a National Disposal Site are dependent upon whether the reactor-produced wastes are reprocessed at the disposal site or are reprocessed elsewhere and shipped to the site. If reprocessed elsewhere the wastes should be solidified prior to shipment, since the shipment of liquid wastes is extremely dangerous. The recommended treatment for the low-level wastes is solidification with asphalt and disposal by land burial. For the high-level reactor-produced wastes the recommended processes are:

Process	Order of Preference	Remarks
Near-surface solid storage	First Choice	Demonstrated technology; waste under constant surveillance and control and can be retrieved.
Salt beds	Second Choice	Affords permanent disposal without constant surveillance; further development required for a waste retrieval plan and location of an acceptable site.

For each of these processes the wastes should be solidified following the reprocessing step by spray solidification.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Ruthenium-106

Half-life 368 days

Type of Decay Negative Beta

Structural Formula

$_{44}Ru^{106}$

Molecular Wt. 106 Melting Pt. 2250 C Boiling Pt. 3900 C

Density 12.30 gm/cm^3 Specific Power 33.1 watts/gm

Specific Activity 3,360 curies/gm

Solubility

Cold Water Insoluble Hot Water Insoluble

Others: Insoluble in aqua regia, acid & alcohol; soluble in fused alkali

Decay Chain

$$\underset{(368d)}{Ru^{106}} \xrightarrow{B^-} \underset{(30s)}{Rh^{106}} \xrightarrow{B^-} \underset{(stable)}{Pd^{106}}$$

Radiation Energy Level & Intensities

Ruthenium-106

Beta: 0.0392 Mev (max)
Gamma: None

Rhodium-106

Beta: 3.55 Mev (90%)
3.10 Mev (3%)
2.40 Mev (5%)
Gamma: 0.512 Mev (21%)
0.622 Mev (1%)
1.050 Mev (1.5%)

Shipping Regulations by the Department of Classified as a transport group III radionuclide Transportation

Comments

References: (1) 0766
(2) 2150

HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Cerium-144

Half-life 284 days

Type of Decay Negative Beta

Structural Formula

$_{58}Ce^{144}$

Molecular Wt. 144

Melting Pt. 795 C

Boiling Pt. 3468 C

Density 6.78 gm/cc

Specific Power 25.6 watts/gm

Specific Activity 3,180 curies/gm

Solubility

Cold Water Slightly reactive

Hot Water Reacts

Others: Soluble in dilute mineral acid; insoluble in alkali

Decay Chain

$$Ce^{144} \xrightarrow{B^-} Pr^{144} \xrightarrow{B^-} Nd^{144}$$

(284d) (17.3m) (stable)

Radiation Energy Level & Intensities

Cerium-144

Beta: 0.309 Mev (76%)
0.175 Mev (24%)

Gamma: 0.134 Mev (11%)
0.080 Mev (2%)

Praseodymium-144

Beta: 2.996 Mev (max)

Gamma: 2.186 Mev (0.7%)
1.487 Mev (0.3%)
0.695 Mev (1.5%)

Shipping Regulations Classified as a transport group III radionuclide by the Department of Transportation

Comments

References:
(1) 0766
(2) 2147
(3) 2150

HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Promethium-147

Half-life 2.62 years

Type of Decay Negative beta

Structural Formula

$_{61}Pm^{147}$

Molecular Wt. 147   Melting Pt. 1035 C   Boiling Pt. 2730 C

Density 7.3 gm/cm^3 Specific Power 0.33 watts/gm

Specific Activity 929 curies/gm

Solubility

Cold Water ____   Hot Water ____

Others: ____

Decay Chain

$Pm^{147} \xrightarrow{B^-} Sm^{147}$

(2.62y) (stable)

Radiation Energy Level & Intensities

Beta: 0.224 Mev (100%)

Gamma: None

Shipping Regulations Classified as a transport group IV radionuclide by the Department of Transportation

Comments Very limited chemical and physical data. Is a member of the rare-earth group.

References: (1) 2147
(2) 2150

TABLE 1

ANNUAL PRODUCTION OF RUTHENIUM-106 FROM THE CIVILIAN NUCLEAR POWER PROGRAM [705]

Light-Water Reactor Fuels

Annual Production	Calendar Year 1970	1980	1985	1990	2000	2020
grams/year	$.071\times10^5$	4.06×10^5	7.30×10^5	8.26×10^5	6.55×10^5	19.2×10^5
curies/year	$.024\times10^9$	1.36×10^9	2.45×10^9	2.77×10^9	2.19×10^9	6.45×10^9
watts/year	$.141\times10^4$	8.05×10^4	14.5×10^4	16.4×10^4	13.0×10^4	38.2×10^4

Fast-Breeder Reactor Fuels

Annual Production	Calendar Year 1970	1980	1985	1990	2000	2020
grams/year			1.37×10^5	8.26×10^5	35.3×10^5	$106\text{X}10^5$
curies/year			0.46×10^9	2.77×10^9	11.8×10^9	35.6×10^9
watts/year			2.73×10^4	16.5×10^4	70.2×10^4	211×10^4

TABLE 2

ANNUAL PRODUCTION OF CERIUM-144 FROM THE CIVILIAN NUCLEAR POWER PROGRAM[705]

Light-Water Reactor Fuels

Annual Production	1970	1980	1985	1990	2000	2020
			Calendar Year			
grams/year	$.15\times10^5$	8.26×10^5	14.9×10^5	16.8×10^5	13.3×10^5	39.2×10^5
curies/year	$.046\times10^9$	2.64×10^9	4.75×10^9	5.38×10^9	4.26×10^9	12.5×10^9
watts/year	$.041\times10^6$	2.31×10^6	4.17×10^6	4.72×10^6	3.74×10^6	11.0×10^6

Fast-Breeder Reactor Fuels

Annual Production	1970	1980	1985	1990	2000	2020
			Calendar Year			
grams/year			1.43×10^5	8.6×10^5	36.7×10^5	110×10^5
curies/year			$.46\times10^9$	2.75×10^9	11.8×10^9	35.3×10^9
watts/year			$.40\times10^6$	2.41×10^6	10.3×10^6	30.9×10^6

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TABLE 3

ANNUAL PRODUCTION OF PROMETHIUM-147 FROM THE CIVILIAN NUCLEAR POWER PROGRAM [705]

Light-Water Reactor Fuels

Annual Production	Calendar Year 1970	1980	1985	1990	2000	2020
grams/year	$.058 \times 10^5$	3.32×10^5	5.97×10^5	6.75×10^5	5.35×10^5	15.7×10^5
curies/year	$.054 \times 10^8$	3.08×10^8	5.54×10^8	6.27×10^8	4.97×10^8	14.6×10^8
watts/year	$.028 \times 10^5$	1.58×10^5	2.85×10^5	3.23×10^5	2.56×10^5	7.52×10^5

Fast-Breeder Reactor Fuels

Annual Production	Calendar Year 1970	1980	1985	1990	2000	2020
grams/year			1.36×10^5	8.17×10^5	34.9×10^5	$10^5 \times 10^5$
curies/year			1.26×10^8	7.59×10^8	32.4×10^8	97.4×10^8
watts/year			$.65 \times 10^5$	3.91×10^5	16.7×10^5	50.2×10^5

TABLE 4

ACTIVITY OF RUTHENIUM-106, CERIUM-144, AND PROMETHIUM-147 PRODUCTS IN SPENT REACTOR WASTES[705]

Light-Water Reactor Fuels
(Fuel Exposed to 33MWD/Tonne* at 30 MW/Tonne)

Fission Products		After 1 year			After 10 years	
	Grams/Tonne	Watts/Tonne	Curies/Tonne	Grams/Tonne	Watts/Tonne	Curies/Tonne
Ru^{106} - Rh^{106}	81	2,656	546,000	0.16	5	1,100
Ce^{144} - Pr^{144}	143	3,800	912,000	0.05	1.5	300
Pm^{147}	92	44	85,000	8	4	8,000
Other Fission Products	34,784	3,500	679,000	35,002	1,019	307,600

Fast Breeder Reactor Fuels
(Fuel Exposed to 33 MWD/Tonne at 58 MW/Tonne)

Fission Products		After 1 year			After 10 years	
	Grams/Tonne	Watts/Tonne	Curies/Tonne	Grams/Tonne	Watts/Tonne	Curies/Tonne
Ru^{106} - Rh^{106}	204	6,660	1,370,000	0.41	14	2,760
Ce^{144} - Pr^{144}	177	4,700	1,128,000	0.06	2	370
Pm^{147}	300	150	279,000	28	13	26,000
Other Fission Products	34,219	2,290	653,000	34,872	737	251,870

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*Tonne is a metric ton of reactor fuel

TABLE 5

RADIATION PROTECTION STANDARDS FOR INDIVIDUALS AND POPULATION GROUPS

FOR EXTERNAL AND INTERNAL EXPOSURE[2149]

Type of Exposure	Dose to Individuals at Points of Maximum Probable Exposure (rem per year)	Average Dose to a Suitable Population Sample (rem per year)
Whole body, gonads, or bone marrow	0.5	0.17
Thyroid or bone	1.5	0.5
Bone (alternate standards)	Body burden at 0.003 micrograms of radium 226 or its biological equivalent	Body burden of 0.001 micrograms of radium 226 or its biological equivalent

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PROFILE REPORT

Strontium-90 (Yttrium-90)

1. GENERAL

Introduction

Strontium-90 is a radioactive isotope principally produced by the fission of uranium and plutonium. It has a half-life of 28 years and emits a 0.546 Mev beta particle. Strontium-90 produces a short half-lived daughter, yttrium-90. It has a half-life of 64 hours and emits a 2.27 Mev beta particle. Yttrium-90, in turn, produces zirconium-90 which is a stable element.

Strontium-90 has attracted great interest as a public health hazard since it is the most biologically significant of the radioactive fission products produced in either nuclear weapon tests or nuclear reactors. Its biological significance is derived from several factors: (1) it has a large fission yield (5.9%); (2) it has a long effective half-life; (3) it tends to deposit and concentrate in the bone tissue (due to the fact that strontium is chemically similar to calcium). In the wastes generated at nuclear power plants strontium-90 and its daughter yttrium-90 are responsible for approximately 7 percent and 38 percent of the total fission product activity in the wastes after 1 year and 10 years, respectively.

The projected growth in the production of strontium-90 will parallel that of the civilian nuclear power program. Present projections indicate that the total installed capacity of nuclear power plants will grow by a factor of 60 between 1970 and 1985.[2148] Projected annual production figures from the civilian nuclear power program for strontium-90 to the year 2020 for light-water and fast-breeder reactor fuels are attached (Table 1). The expected total accumulated radioactivity for strontium-90 from the year 1970 to 2020 in millions of curies is:

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Year	Radioactivity (Megacuries)
1970	4
1980	962
1990	4,640
2000	9,550
2020	29,400

These figures along with the annual production figures illustrate the tremendous growth anticipated in the production of this isotope. Annual production figures or accumulated totals for strontium-90 produced as part of the nuclear weapons program were not available.

Manufacture

Strontium-90 is produced by the fission of the heavy elements, i.e., those elements heavier than lead. The fission reaction results from neutron bombardment or spontaneous decomposition of the nucleus. A typical fission reaction is:

$$_{92}U^{235} + {}_{o}n^{1} \rightarrow {}_{38}Sr^{90} + {}_{54}Xe^{144} + 2{}_{o}n^{1}$$

Presently, strontium-90 is produced in thermal power reactors by the fission of uranium. Civilian nuclear power plants are the major producers and a smaller amount is produced at AEC facilities. At the present time there are 22 nuclear power plants in operation with an additional 104 being built or planned.[2151] In the future, strontium-90 will also be produced in fast-breeder reactors by the fission of plutonium.

Uses

Strontium-90 is one of the best long-lived high-energy beta emitters known. It is used in military and space applications as an energy source for small auxiliary power units. It also is used in the radioactive gauge field. Beta gauges activated by strontium-90 are extensively used in industry to measure and control the thickness or density of thin materials (paper, textiles, etc.) or coatings. In the field of nuclear medicine strontium-90 is used as a source of beta radiation for the treatment of skin diseases and eye disorders and also as a medical blood irradiator. At the present time the strontium-90 used in the above applications is obtained from the waste streams in the Richland, Washington, chemical separations plant and is distributed through the Oak Ridge National Laboratory, Isotopes Sales Department. In the future, when its production is warranted by market demands, it could be available in large quantities from commercial firms operating chemical processing plants. The AEC revenue from the distribution of strontium-90 through the fiscal years 1965 to 1971 is [2151]:

Year	Revenue (Dollars)
1965	3,000
1966	65,000
1967	59,000
1968	188.000
1969	169,000
1970	72,000
1971	248,000

These figures illustrate the fluctuating nature of the commercial market for the use of strontium-90.

Sources and Types of Strontium-90 Wastes

The primary source of the strontium-90 waste streams are generated at the spent reactor reprocessing plants. Strontium-90 and the other resultant high-level wastes are contained in the aqueous effluent from the reprocessing step. The range of chemical compositions of the various types of waste streams obtained from the reprocessing step have been tabulated,[0715] and in all cases are primarily aqueous solutions of inorganic nitrate salts. Strontium-90 is normally found in the waste stream in the form of a nitrate or oxide. The activity of strontium-90 products in the spent reactor wastes at two different time periods is attached (Table 2).

Strontium-90 is also found in the low and intermediate waste streams generated at fuel reprocessing facilities. The strontium-90 activity in these waste streams is from a few hundredths to several tenths of a curie per gallon of waste. Strontium-90 is also found in the wastes resulting from research laboratories and medical and industrial applications. Generally the strontium-90 waste from these sources is found in the solid form.

Physical and Chemical Properties

The physical and chemical properties of strontium-90 and its short half-lived daughter yttrium-90 are included in the attached worksheet. Strontium-90 is a member of the alkaline-earth metal group. It is a highly metallic and highly electropositive element with a valence of +2. It dissolves readily in acids and will burn when heated in air, oxygen, or carbon dioxide. At low temperatures, oxidation is slow owing to the formation of a protective oxide film. Strontium-90 reacts readily with water, releasing hydrogen and forming metal and hydroxyl ions. The carbonates and sulfates of strontium are very insoluble. The fluorides and the oxalate of strontium are also insoluble. The sulfides, however, are soluble in water.

2. RADIATION HAZARD

Strontium-90 is a very dangerous radioactive material. It tends to concentrate in the bone and irradiate the adjacent soft tissue. The symptoms of strontium-90 radiation exposure are nausea and fatigue followed by vomiting and diarrhea. The possible types of injury include: leukopenia, anemia, leukemia, cataracts, and increases in the average rate of genetic mutation. The effects of strontium-90 radiation exposure are primarily dependent on the amount of radiation and the portion of the body affected. The effects of acute whole-body radiation exposure are: (1) 0 to 25 rem, no detectable clinical effects; (2) 25 to 200 rem, delayed effects and possible shortened life expectancy of 1 percent; (3) 200 to 600 rem, possible premature death; (4) greater than 600 rem, death. These effects are for a single large dose of radiation or a series of substantial doses in a short interval of time to the total body. Standards for prolonged exposure over a fifty-year period have defined the single dose limit in terms of the maximum permissible dose accumulated in a period of 13 weeks. The whole body exposure limit is 3 rem per quarter and the accumulated dose limit is 5(N - 18), where N is the individual's age in years. Limits for the thyroid, bone, and other organs have also been defined.[0563]

Following the inhalation of 1 microcurie of strontium-90 in the insoluble form the critical organ is the bone and the dose delivered to the bone following the inhalation of 1 microcurie of strontium-90 is 56 rem. The dose delivered to the bone following injection of 1 microcurie into the body via a wound is 90 rem. Values of the maximum permissible total body burden of strontium-90 which are deposited in the total body and produces the maximum permissible dose rate to a particular body organ have been compiled.[0563] The maximum permissible body burden for the bone is 2.0 microcuries and for the total body 20 microcuries. The above body burden rates can be expressed in terms of the maximum permissible concentrations of strontium-90 in air and water. These concentrations can be expressed in terms of a daily intake of air and water at the continuous exposure rate of 168 hours per week for a period of 50 years. For strontium-90 the critical organ is the bone and the maximum permissible concentration in water is 1×10^{-6} microcuries per milliliter and in air 1×10^{-10} microcuries per milliliter.[0563]

3. OTHER HAZARDS

Strontium-90 resembles calcium in its metabolism and behavior. Strontium-90, besides its radiation hazard, is moderately toxic to the skin or mucous membranes following a single exposure. Its fire and explosive hazard is moderate, in the form of dust, when exposed to flame or chemical reaction.[0766] It reacts with water to evolve hydrogen. Strontium nitrate or peroxide are powerful oxiding materials. In contact with easily oxidizable substances they react rapidly to cause ignition or explosion by friction or on contact with a small amount of water.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Since strontium-90 is hazardous to man by inhalation, ingestion, or direct radiation exposure, great care must be exercised in its handling. Handling must be set up to prevent excessive exposure to personnel and in fact to prevent any unnecessary exposure. Special procedures and adequate radiation shielding are required in the handling of strontium-90. The beta particles emitted by strontium-90 generally cannot penetrate more than one centimeter or so of metal or glass. The principal shielding problem associated with the beta radiation is the bremsstrahlung effect which results from the presence of highly penetrating rays resulting from the deflection of beta particles by the nuclei in the shielding medium. Since the bremsstrahlung effect increases with atomic number, shielding materials of high atomic weight are not satisfactory. Lead and high-density concrete are commonly used shielding materials for strontium-90 radiation. To detect and control personnel exposure to strontium-90 radiation all persons working with this material should wear an external dosimetry device. The commonly used devices are the film badge and the thermoluminescent dosimeters (TLD).

Strontium-90 should be stored in controlled reservations in specially constructed containers or storage bins. The strontium-90 should be protected by both a primary and a secondary containment barrier. Special monitoring systems and proper warning signs should be located in the general area of the storage facility.

Strontium-90 is classified as a transport group II radionuclide by the Department of Transportation, and the rules and regulations governing their transportation are given in the Code of Federal Regulations (CFR) Title 49--Transportation, Parts 170 to 190.[2150] The strontium-90 content is limited to 0.05 curies for a Type A package and 20 curies for a Type B package defined in 49CFR173. The limits are increased to 20 and 500 curies if the physical form of the strontium-90 meets the requirements of a special form material. The strontium-90 release rate is limited to zero under the specified accident conditions for Type A and B quantities.[2150] The allowable release of radioactivity from packages containing large quantities of strontium-90 is limited to gases and contaminated coolant containing total radioactivity exceeding neither 0.1 percent of the total radioactivity of the package nor 0.5 curies under the hypothetical accident conditions prescribed in 49CFR173.

Disposal/Reuse

The disposal of strontium-90 is governed by the AEC Manual Chapter 0524[0559] and 10CFR20.[2149] Two sets of standards have been established for the permissible radiation exposure in unrestricted areas. One is for the greatest dose received by an individual and the other for the average dose received by the general population. The radiation protection standards for these two groups is attached. The standards for the safe disposal of strontium-90 also define its maximum concentrations in air and water. The safe release of strontium-90 to the environment in an unrestricted area should not exceed the concentration in microcuries per milliliter (uc/ml) listed below[2149]:

Exposure Group	Strontium-90 Form	Concentration in Air	Concentration in Water
Individual	Soluble	3×10^{-11} uc/ml	3×10^{-7} uc/ml
Individual	Insoluble	2×10^{-10} uc/ml	4×10^{-5} uc/ml
Population	Soluble	1×10^{-11} uc/ml	1×10^{-7} uc/ml
Population	Insoluble	$.67\times10^{-10}$ uc/ml	1.3×10^{-5} uc/ml

The disposal of strontium-90 by release into a sanitary sewage system is limited to 1 microcurie or a concentration of 1×10^{-5} microcuries per milliliter of water in the soluble form or 1×10^{-3} microcuries per milliliter of water in the insoluble form. The disposal of strontium-90 by burial in the soil at any one location and time is limited to 100 microcuries of strontium-90.[2149]

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Recovery

Option #1 - Precipitation. Strontium-90 can be removed from high-level reactor wastes following the reprocessing step by precipitating as a carbonate or flouride[0686] or absorbing on alumino-silicate zeolites.[0738] The standard procedure for the recovery of strontium-90 is to precipitate as a carbonate and then add titanium dioxide and heat to drive off the CO_2, forming strontium titanite. The strontium-90 can be recovered from the other high-level reactor wastes for commercial purposes, or to provide isolation of the strontium-90 for heat transfer and safety reasons (see radioactive waste solidification report).

Option #2 - Scavenging-Precipitation Foam Separation. The removal of strontium-90 from radioactive waste water by scavenging-precipitation foam separation has been studied by Oak Ridge National Laboratory.[0703] The process consists of two steps: (1) precipitating in a sludge blanket clarification step, and (2) achieving final decontamination in a foam-separation column. Processing rates of 300 gal per hour (gph) for scavenging precipitation and 120 gph for foam separation have been achieved. Strontium-90 is precipitated by the addition of calcium carbonate or calcium phosphate. Strontium-90 decontamination factors (ratio of initial to final concentration) of 1050 have been obtained.[0703] At the present time, further development is required to reduce operating costs and increase processing rates.

Option #3 - Scavenging-Precipitation Ion Exchange. In this process final decontamination is obtained by ion exchange columns from the scavenging-precipitation process. In the phenolic ion exchange column calcium and magnesium are removed with the strontium. The process includes a provision for the recycle of the ion exchange waste to the scavenging-precipitation step. All the removed radionuclides are concentrated in the clarifier sludge. The overall decontamination factors for strontium-90 varied from 1,200 to 12,000.[0705] The use of ion exchange resins with a scavenging-precipitation step is a fairly simple and efficient means of removing strontium-90 from low-level radioactive aqueous wastes.

Option #4 - Water Recycle. The water recycle process is used for decontaminating radioactive waste water and recycling the purified water for reuse. This process has been demonstrated at the pilot plant scale by Oak Ridge National Laboratory.[0707] The steps in the process include: (1) clarification by controlled addition of coagulants; (2) demineralization by cation-anion exchange; and (3) sorption on granular activated carbon. The majority of the strontium-90 is removed by the cation-anion exchange. The strontium-90 overall decontamination factor was 5,700. The method is an improvement to the treat-and-discharge methods, but further work is required until full-scale production use is obtained.

Disposal

Option #1 - Land Burial. Land burial of strontium-90 wastes, in small concentrations, at approved sites that are acceptable from a geologic and hydrologic standpoint, is an acceptable means of disposal. Strontium-90 concentration should not be in excess of 10^4 times the maximum permissible concentration for the general population in 10CFR20.[2149] All strontium-90 wastes to be disposed of should be in a solid form and encapsulated in a suitable container. Liquid strontium-90 wastes should be solidified, preferably using asphalt, in accordance with the methods described in the radioactive waste solidification report. The burial trenches should be designed not to intercept the ground water table and constructed with a bottom drain and sump for water monitoring. The trenches should be covered with either asphalt or vegetation to prevent infiltration of water. The burial site design, geology, and hydrology should be in conformance with the criteria used in selecting and licensing the present commercial burial sites.[1423] Since land burial has successfully been practiced on a commercial scale, it should be considered as the most satisfactory method of disposing of all dilute concentrations of strontium-90 wastes.

Option #2 - Near-Surface Liquid Storage. Near-surface storage of reactor produced liquid strontium-90 wastes in stainless steel tanks encased in concrete and buried underground is not considered as a satisfactory means of disposal. Liquid reactor wastes have been stored in this manner over the past 25 years. The tanks range in size from 0.33 to 1.3 million gallons and are generally equipped with devices for measuring temperatures, liquid levels, and leaks. At the present time these tanks are considered as an interim storage technique due to a general lack of confidence in their long-term integrity.[0705] In addition, present regulations require the solidification of all reactor wastes within 5 years following reprocessing.[2149] Therefore, the near-surface storage of liquid strontium-90 wastes in steel tanks should only be considered as a near-term storage technique and not as a permanent storage or disposal technique.

Option #3 - Near-Surface Solid Storage. The disposal of high-level solidified strontium-90 wastes in engineered surface facilities offers the best immediate method for disposal of these wastes. The technology for these facilities has been developed and the wastes will be under surveillance and control and can be retrieved, should this be required. The reactor-produced wastes should be solidified and encapsulated in a suitable container (stainless steel). Of the four high-level solidification processes developed, spray solidification offers the best solidified waste characteristics (see radioactive waste solidification report). The wastes will be stored in stainless steel vaults encased in concrete. The vaults will be either air or water cooled. Corrosion of the waste containers will require their periodic replacement. For strontium-90 this will be required since its activity is only reduced by a factor of 10 in 100 years.

Option #4 - Salt Deposits. This method offers the greatest potential for the disposal of reactor-produced strontium-90 wastes since bedded salt deposits are completely free of circulating ground waters. This method of disposal has been under study by the Oak Ridge National Laboratory since 1957, and in November of 1970 a committee of the National Academy of Sciences recommended that the use of bedded salt for the disposal of radioactive wastes is satisfactory.[0733] The reactor-produced strontium-90 wastes must be solidified and disposed of in the solid form encapsulated in a suitable container. The preferred solidification process is spray solidification. The solidified wastes are then buried in rooms carved in the salt deposits approximately 1,000 feet below the ground. The salt is a good heat transmitter, provides about the same radioactive shielding as concrete, and can heal its own fractures by plastic flow. The critical problem is the selection of a site that meets the necessary design and geological criteria. For strontium-90 wastes the life of the mine must extend beyond a few hundred years. Salt deposits should be considered for the disposal of strontium-90 wastes at approved sites that are acceptable from a design and geological standpoint. In addition, a method of waste retrieval is required in the event the integrity of the site is destroyed.

Option #5 - Bedrock Disposal. The disposal of liquid strontium-90 wastes along with other spent reactor wastes in vaults excavated in crystalline rock over 1,500 feet beneath the ground is currently being evaluated by E. I. du Pont de Nemours, at their Savannah River Plant near Aiken, South Carolina.[0894, 1396] The wastes would be stored in six tunnels and once in the tunnels the wastes will seep into the surrounding rock. Located above the crystalline rock is the Tuscaloosa formation, a good source of freshwater, which is separated by a layer of clay that would act as a barrier to the leakage of radioactive wastes. An advisory committee appointed by the National Academy of Sciences recommended abandonment of the project. In May 1972, another National Academy of Sciences panel concluded that bedrock storage provides a reasonable prospect for long-term safe storage, but an unprecedented degree of precise information is needed to decide if and where underground storage vaults should be built. Another method has also been proposed for disposing of liquid wastes by in situ incorporation in molten silicate rock.[2146] At the present time both of these methods are unsatisfactory since sufficient engineering data or exploration has not been completed to verify their suitability. Due to the long half-life and high biological hazard of strontium-90, it is doubtful that data could ever be accumulated to prove that the geological characteristics of the site over the next few hundred years are acceptable to ensure the absolute safety of such a disposal method.

Option #6 - Hydraulic Fracturing. The direct disposal of aqueous intermediate-level radioactive wastes into shale formations has been investigated by Oak Ridge National Laboratory.[0709] The method consists of mixing the aqueous wastes with cement and pumping the resulting slurry down a well out into a nearly horizontal fracture in a thick shale formation. Since strontium-90 is leached from cement and no additional encapsulation is provided, this method of disposal is not satisfactory.

To summarize, strontium-90 can be recovered from the high-level reactor waste streams for separate disposal or reuse. The separation of strontium-90 from these waste streams will probably be required with the introduction of the fast-breeder reactor due to its high heat content (see radioactive waste solidification report). The acceptable method of treatment is spray solidification and disposal in either salt deposits or near-surface engineered facilities. Strontium-90 should be recovered from the low-level waste streams to minimize the amount directly released to the environment. An adequate method of recovery is scavenging-precipitation ion exchange. The recovered strontium-90 can then be solidified, preferably using asphalt, and disposed of at approved sites by land burial.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Strontium-90 is a candidate for a National Disposal Site due to its health hazard and its projected growth with that of the civilian nuclear power program. The applicability of the recovery processes to a National Disposal Site are dependent upon whether the reactor-produced strontium-90 wastes are reprocessed at the disposal site or are reprocessed elsewhere and shipped to the site. If reprocessed elsewhere the wastes should be solidified prior to shipment, since the shipment of liquid wastes is extremely dangerous. From a cost and safety viewpoint, it would be desirable to combine the reprocessing plant and the National Disposal Site. Disposal in near-surface engineered facilities offers considerable latitude in the disposal site selection, whereas site selection would be seriously limited with salt mine disposal.

The recommended treatment for low-level strontium-90 waste streams is recovery by scavenging-precipitation ion exchange followed by solidification with asphalt and disposal by land burial. For the high-level, reactor-produced strontium-90 wastes, the recommended processes are:

Process	Order of Preference	Remarks
Near-surface solid storage	First choice	Demonstrated technology; waste under constant surveillance and control and can be retrieved.
Salt beds	Second choice	Affords permanent disposal without constant surveillance; further development required for a waste retrieval plan and location of an acceptable site.

For each of these processes the wastes should be solidified following the reprocessing step by spray solidification.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Strontium-90

Half-life 28 years

Type of Decay Negative Beta

Structural Formula

$_{38}Sr^{90}$

Molecular Wt. 90 Melting Pt. 769C Boiling Pt. 1384C

Density 2.6 gm/cc Specific Power 0.98 watts/gm

Solubility Specific Activity 142 curies/gm

Cold Water Reacts Hot Water Reacts

Others: Soluble in acid, alcohol, and liquid NH_3

Decay Chain

$$\underset{(28y)}{Sr^{90}} \xrightarrow{B^-} \underset{(64h)}{Y^{90}}$$

Radiation Energy Level & Intensities

Beta: 0.549 Mev (100%)

Gamma: None

Shipping Regulations Classified as a transport group II radionuclide by the Department of Transportation

Comments

References: (1) 0766
(2) 2147
(3) 2150

HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Yttrium-90

Half-life 64 hours

Type of Decay Negative Beta

Molecular Wt. 90 Melting Pt. 1495C Boiling Pt. 2927C

Density 4.34

Structural Formula

$_{39}Y^{90}$

Specific Power

Specific Activity 5.3×10^{5} curies/gm

Solubility

Cold Water Slightly reactive Hot Water Reacts

Others: Very soluble in dilute acid; soluble in hot KOH

Decay Chain

$$\underset{(64h)}{Y^{90}} \xrightarrow{B^-} \underset{(Stable)}{Zr^{90}}$$

Radiation Energy Level & Intensities

Beta: 2.27 Mev(max)

Gamma: None

Shipping Regulations Classified as a transport group IV radionuclide by the Department of Transportation

Comments

References: (1) 0766
(2) 2150
(3)

TABLE 1

ANNUAL PRODUCTION OF STRONTIUM-90 FROM THE CIVILIAN NUCLEAR POWER PROGRAM [705]

Light-Water Reactor Fuels

	Calendar Year					
Annual Production	1970	1980	1985	1990	2000	2020
grams/year	2.83×10^4	161×10^4	291×10^4	328×10^4	260×10^4	764×10^4
curies/year	4.0×10^6	228×10^6	410×10^6	463×10^6	367×10^6	1080×10^6
watts/year	$.52 \times 10^4$	29.6×10^4	53.3×10^4	60.30×10^4	47.8×10^4	140.5×10^4

Fast-Breeder Reactor Fuels

	Calendar Year			
Annual Production	1985	1990	2000	2020
grams/year	11×10^4	66×10^4	282×10^4	846×10^4
curies/year	15.5×10^6	93.4×10^6	399×10^6	1200×10^6
watts/year	2.0×10^4	12.2×10^4	52×10^4	156×10^4

TABLE 2

ACTIVITY OF STRONTIUM-90 PRODUCTS IN SPENT REACTOR WASTES [705]

Light-Water Reactor Fuels

(Fuel Exposed to 33 MWD/Tonne* at 30 MW/Tonne)

Fission	After 1 year			After 10 years		
Products	Grams/Tonne	Watts /Tonne	Curies/Tonne	Grams/Tonne	Watts /Tonne	Curies/Tonne
Sr^{90} - Y^{90}	534	530	151,000	427	425	120,900
Other Fission Products	34,566	9,470	2,071,000	34,673	605	196,100

Fast-Breeder Reactor Fuels

(Fuel Exposed to 33 MWD/Tonne at 58 MW/Tonne)

Fission	After 1 year			After 10 years		
Products	Grams/Tonne	Watts/Tonne	Curies/Tonne	Grams/Tonne	Watts/Tonne	Curies/Tonne
Sr^{90} - Y^{90}	300	298	85,000	241	239	68,000
Other Fission Products	34,600	13,502	3,345,000	34,658	529	213,000

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*Tonne is a metric ton of reactor fuel

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TABLE 3

RADIATION PROTECTION STANDARDS FOR INDIVIDUALS AND POPULATION GROUPS

FOR EXTERNAL AND INTERNAL EXPOSURE [2149]

Type of Exposure	Dose to Individuals at Points of Maximum Probable Exposure (rem per year)	Average Dose to a Suitable Population Sample (rem per year)
Whole body, gonads, or bone marrow	0.5	0.17
Thyroid or bone	1.5	0.5
Bone (alternate standards)	Body burden at 0.003 micrograms of radium 226 or its biological equivalent	Body burden of 0.001 micrograms of radium 226 or its biological equivalent

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PROFILE REPORT

Zirconium-95, Niobium-95

I. GENERAL

Zirconium-95 is a radioactive isotope principally produced in nuclear reactors by the fission of uranium and plutonium. Zirconium-95 has a half-life of 65 days and emits both beta particles and gamma rays. Zirconium-95 produces, by beta decay, niobium-95. Niobium-95 has a half-life of 35 days, emits a 0.160 Mev beta particle and a 0.765 Mev gamma ray. Niobium-95 is transformed by beta decay into molybdenum-95 which is a stable element.

Zirconium-95 and niobium-95 are both short-lived isotopes and account for 25 percent of the total activity in spent reactor wastes after 90 days. Their activity decreases to less than 1 percent of the total after 1 year. They also present considerable difficulty in the separation of uranium and plutonium from these elements since they both form radioactive colloids in solution. Besides the erratic behavior of these colloids during reprocessing, they also tend to be absorbed on surfaces such as container walls.

The projected growth in zirconium-95 and niobium-95 will parallel that of the civilian nuclear power program. Present projections indicate that the total installed capacity of nuclear power plants will grow by a factor of 60 between 1970 and 1985.[2148] Projected annual production figures from the civilian nuclear power program for these two isotopes to the year 2020 for light-water and fast-breeder reactor fuels are attached (Tables 1 and 2). These figures illustrate the tremendous growth anticipated in their production but their commercial use is very limited.

The primary source of zirconium-95 and niobium-95 wastes are generated at the spent reactor fuel reprocessing plants. These isotopes and the other resultant high-level reactor wastes are contained in the aqueous effluent from the reprocessing step. The range of chemical compositions of the various types of waste streams obtained from the reprocessing step have been tabulated. 0715 The activity of zirconium-95 and niobium-95 in the spent reactor wastes at two different times is attached (Tables 3 and 4). Due to their short half-life, their activity after 10 years is reduced to zero. They are also found in very small quantities in the secondary waste streams generated at fuel reprocessing facilities.

The physical and chemical properties of zirconium-95 and niobium-95 are included in the attached worksheets. Zirconium-95 is a member of the group IV series of metals, all of which have a characteristic +4 oxidation state. Zirconium-95 is not readily soluble in nitric acid but dissolves at substantial rates in both hydrofluoric and moderately concentrated sulfuric acid. Niobium-95 exists in the +5 oxidation state in a majority of its compounds. Niobium-95 is a passive metal and does not dissolve in most acids when pure, but is attacked by these acids if impurities are present. Both isotopes tend to form radioactive colloids in solution which do not act as true solutes but tend to be absorbed on surfaces.

2. RADIATION HAZARD

Zirconium-95 and niobium-95 are both moderately dangerous radioactive materials. Zirconium-95 is classified as a slightly more hazardous material than niobium-95. The effects of their radiation are primarily dependent on the amount of radiation and the portion of the body affected. The effects of acute whole-body radiation exposure are: (1) 0 to 25 rem, no detectable clinical effects; (2) 25 to 200 rem, delayed effects and possible shortened life expectancy of 1 percent; (3) 200 to 600 rem, death. These effects are for a single large dose of radiation or a series of substantial doses in a short interval of time to the total body. Standards for prolonged exposure over a fifty-year period have defined the single dose limit in terms of the maximum permissible dose accumulated in a period of 13 weeks. The whole body exposure limit is 3 rem per quarter and the accumulated dose limit is 5(N-18), where N is the individual's age in years. Limits for the thyroid, bone, and other organs have been defined.[0563]

The zirconium-95 dose in the insoluble form to the lung is 0.22 rem following the inhalation of 1 microcurie. In the soluble form the dose delivered to the bone following the inhalation of 1 microcurie of zirconium-95 is 0.06 rem. The dose delivered to the bone following injection of 1 microcurie into the body via a wound is 0.22 rem. For niobium-95 the above doses are reduced by a factor of three to four.

Values of the maximum permissible total body burden of zirconium-95 and niobium-95 which are deposited in the total body and produce the maximum permissible dose rate to a particular body organ have been compiled.[0563] For both isotopes the critical organ is the bone and the maximum permissible body burden is 20 microcuries for zirconium-95 and 40 microcuries for niobium-95.

3. OTHER HAZARDS

Besides its radiation hazard, zirconium-95 is not an important poison, and so far as is known, the inherent toxicity of zirconium compounds is low.[0776] The toxicity of niobium is unknown.[0776] Zirconium fire and explosive hazard is high, especially in the form of dust when exposed to chemical reaction with air or oxidizing agents. The fire and explosive hazard of niobium is low.

4. DEFINITION OF ADEQUATE WASTE MANAGEMENT

Handling, Storage, Transportation

Since zirconium-95 and niobium-95 are hazardous to man by inhalation ingestion, or direct radiation exposure, great care must be exercised in their handling. Handling must be set up to prevent excessive exposure to personnel and in fact to prevent any unnecessary exposure. Special procedures and adequate radiation shielding are required in their handling. The beta particles emitted by them generally cannot penetrate more than 0.1 in. of water or 0.04 in. of glass. Their gamma rays are highly penetrating. Lead and concrete are commonly-used shielding materials. To detect and control personnel exposure, all persons working with these materials should wear an external dosimetry device. The commonly used devices are the film badge and the thermoluminescent dosimeters (TLD).

Zirconium-95 and niobium-95 should be stored in controlled reservations in specially constructed containers or storage bins. They should be protected by both a primary and a secondary containment barrier. Special monitoring systems and proper warning signs should be located in the general area of the storage facility.

Zirconium-95 is classified as a transport group III and niobium-95 as a transport group IV radionuclide by the Department of Transportation, and the rules and regulations governing their transportation are given in the Code of Federal Regulations (CFR) Title 49--Transportation, Parts 170 to 190.[2150] The zirconium-95 content is limited to 3 curies for a Type A package and 200 curies for a Type B package defined in 49CFR173. For niobium-95 the limits are 20 curies for a Type A package and 200 curies for a Type B package. The limits are increased to 20 and 5,000 curies if their physical form meets the requirements of a special form material. Their release rate is limited to zero under the specified accident conditions for Type A and B quantities.[2150] The allowable release of radioactivity from packages containing large quantities of these isotopes is limited to gases and contaminated coolant containing total radioactivity exceeding neither 0.1 percent of the total radioactivity of the package nor 10 curies under the hypothetical accident conditions prescribed in 49CFR173.

Disposal/Reuse

The disposal of zirconium-95 and niobium-95 is governed by the AEC Manual Chapter 0524[0559] and 10CFR20.[2149] Two sets of standards have been established for the permissible radiation exposure in unrestricted areas. One is for the greatest dose received by an indiviudal and the other for the average dose received by the general population. The radiation protection standards for these two groups is attached (Table 5). The standards for the safe disposal of zirconium-95 and niobium-95 also define their maximum concentrations in air and water. Their safe release to the environment in an unrestricted area should not exceed the concentrations in microcuries per milliliter included in this report (Table 6).

The disposal of zirconium-95 and niobium-95 into a sanitary sewage system is limited to 100 microcuries. Their disposal by burial in the soil at any one location and time is limited to 10,000 microcuries.[2149]

5. EVALUATION OF CURRENT AND NEAR FUTURE DISPOSAL PROCESSES

Recovery

Option #1 - Scavenging-Precipitation Foam Separation. The removal of zirconium-95 and niobium-95 from low-level radioactive waste water by scavenging-precipitation foam separation has been studied by Oak Ridge National Laboratory.[0703] The process consists of two steps: (1) precipitating in a sludge-blanket clarification step; and (2) achieving final decontamination in a foam-separation column. Processing rates of 300 gal per hour (gph) for scavenging precipitation and 120 gph for foam separation have been achieved. Decontamination factors (ratio of initial to final concentration) greater than 50 have been obtained for both isotopes.[0703] At the present time, further development is required to reduce operating costs and increase processing rates.

Option #2 - Scavenging-Precipitation Ion Exchange. In this process final decontamination is obtained by ion exchange columns from the scavenging-precipitation process. The process includes a provision for the recycle of the ion exchange waste to the scavenging-precipitation step. All the removed radionuclides are concentrated in the clarifier sludge. The overall decontamination factors for these isotopes varied from 10 to 150.[0705] The use of ion exchange resins with a scavenging-precipitation step is a fairly simple and efficient means of removing these isotopes from low-level radioactive aqueous wastes.

Option #3 - Water Recycle. The water recycle process is used for decontaminating radioactive waste water and recycling the purified water for reuse. The process has been demonstrated at the pilot plant scale by Oak Ridge National Laboratory.[0707] The steps in the process include: (1) clarification by the addition of coagulants; (2) demineralization by cation-anion exchange; and (3) sorption on granular activated carbon. Overall decontamination factors of 350 were obtained. This is the minimum value since the concentrations of zirconium-95 and niobium-95 were reduced to the analytical limits of detection (background). This method is an improvement to the treat-and-discharge methods, but further work is required until full-scale production use is obtained.

Disposal

Option #1 - Land Burial. Land burial of zirconium-95 and niobium-95 wastes, in small concentrations, at approved sites that are acceptable from a geologic and hydrologic standpoint, is an acceptable means of disposal. Their concentrations should not be in excess of 10^4 times their maximum permissible concentrations for the general population in 10CFR20.[2149] All wastes to be disposed of should be in a solid form and encapsulated in a suitable container. Liquid wastes should be solidified, preferably using asphalt, in accordance with the methods described in the Radioactive Waste Solidification report. The burial trenches should be designed not to intercept the ground water table and constructed with a bottom drain and sump for water monitoring. The trenches should be covered with either asphalt or vegetation to prevent infiltration of water. The burial site design, geology, and hydrology should be in conformance with the criteria used in selecting and licensing the present commercial burial sites.[1423] Since land burial has successfully been practiced on a commercial scale and both zirconium-95 and niobium-95 have short half-lives, it should be considered as the most satisfactory method of disposing of all dilute concentrations of these wastes.

Option #2 - Near-Surface Liquid Storage. Near-surface storage of reactor-produced liquid zirconium-95 and niobium-95 waste in stainless steel tanks encased in concrete and buried underground is not considered as a satisfactory means of disposal. Liquid reactor wastes have been stored in this manner over the past 25 years. The tanks range in size from 0.33 to 1.3 million gal and are generally equipped with devices for measuring temperatures, liquid levels, and leaks. At the present time these tanks are considered as an interim storage technique due to a general lack of confidence in their long-term integrity.[0705] In addition, present regulations require the solidification of all reactor wastes within 5 years following reprocessing.[2149] Therefore, the near-surface storage of these liquid wastes in steel tanks should only be considered as a near-term storage technique and not as a permanent storage or disposal technique.

Option #3 - Near-Surface Solid Storage. The disposal of high-level solidified zirconium-95 and niobium-95 wastes in engineered surface facilities offers the best immediate method for disposal of these wastes. The technology for these facilities has been developed and the wastes will be under surveillance and control and can be retrieved, should this be required. The reactor-produced wastes should be solidified and encapsulated in a suitable container (stainless steel). Of the four high-level solidification processes developed, spray solidification offers the best solidified waste characteristics (see Radioactive Waste Solidification report). The wastes will be stored in stainless steel vaults encased in concrete. The vaults will either be air or water cooled. The periodic replacement of the waste containers probably will not be required since the activity of zirconium-95 is reduced by a factor of 100 in 432 days and niobium-95 activity is reduced by a factor of 100 in 232 days. The replacement of the containers will be required if other long-lived isotopes are present.

Option #4 - Salt Deposits. This method offers the greatest potential for the disposal of reactor-produced zirconium-95 and niobium-95 wastes since bedded salt deposits are completely free of circulating ground waters. This method of disposal has been under study by the Oak Ridge National Laboratory since 1957, and in November of 1970 a committee of the National Academy of Sciences recommended that the use of bedded salt for the disposal of radioactive wastes is satisfactory.[0733] The wastes must be solidified and disposed of in the solid form, and encapsulated in a suitable container. The preferred solidification process is spray solidification. The solidified wastes are then buried in rooms carved in the salt deposits, approximately 1,000 ft below the ground. The salt is a good heat transmitter, provides about the same radioactive shielding as concrete, and can heal its own fractures by plastic flow. Salt deposits should be considered for the disposal of these wastes at approved sites that are acceptable from a design and geological standpoint.

Option #5 - Bedrock Disposal. The disposal of liquid zirconium-95 and niobium-95 wastes along with other spent reactor wastes in vaults excavated in crystalline rock over 1,500 ft beneath the ground is currently being evaluated by E. I. Du Pont de Nemours, at their Savannah River Plant near Aiken, South Carolina.[0894, 1396] The wastes would be stored in six tunnels and once in the tunnels the wastes will seep into the surrounding rock. Located above the crystalline rock is the Tuscaloosa formation, a good source of freshwater, which is separated by a layer of clay that would act as a barrier to the leakage of radioactive wastes. An advisory committee appointed by the National Academy of Sciences recommended abandonment of the project. In May 1972, another National Academy of Sciences panel concluded that bedrock storage provides a reasonable prospect for long-term safe storage, but an unprecedented degree of precise information is needed to decide if and where underground storage vaults should be built. Another method has also been proposed for disposing of liquid wastes by in situ incorporation in molten silicate rock.[2146] At the present time both of these methods are unsatisfactory since sufficient engineering data or exploration has not been completed to verify their suitability.

Option #6 - Hydraulic Fracturing. The direct disposal of aqueous intermediate-level radioactive wastes into shale formations has been investigated by Oak Ridge National Laboratory. 0709 The method consists of mixing the aqueous wastes with cement and pumping the resulting slurry down a well out into a nearly horizontal fracture in a thick shale formation. Since zirconium-95 and niobium-95 are leached from cement and no additional encapsulation is provided, this method of disposal is not satisfactory.

To summarize, both zirconium-95 and niobium-95 are short-lived isotopes with a high initial activity but whose activity decreases by a factor of 1,000 within 2 years. These isotopes will probably be contained with the long-lived reactor wastes since their recovery is not required due to their short half-life and limited commercial use. The acceptable method of treatment is solidification and disposal in salt deposits or near-surface engineered facilities.

6. APPLICABILITY TO NATIONAL DISPOSAL SITES

Zirconium-95 and niobium-95 are both candidates for a National Disposal Site due to their projected growth with that of the civilian nuclear power program. The applicability of the recovery processes to a National Disposal Site are dependent upon whether the reactor-produced wastes are reprocessed at the disposal site or are reprocessed elsewhere and shipped to the site. If reprocessed elsewhere the wastes should be solidified prior to shipment, since the shipment of liquid wastes is extremely dangerous.

The recommended treatment for low-level zirconium-95 and niobium-95 waste streams is recovery by scavenging-precipitation ion exchange followed by solidification with asphalt and disposal by land burial. For the high-level reactor-produced zirconium-95 and niobium-95 wastes, the recommended processes are:

Process	Order of Preference	Remarks
Near-surface solid storage	First choice	Demonstrated technology; waste under constant surveillance and control and can be retrieved.
Salt beds	Second choice	Affords permanent disposal without constant surveillance; further development required in the selection of a site that meets the necessary design and geological criteria.

For each of these processes the wastes should be solidified following the reprocessing step by spray solidification.

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HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Zirconium-95

Half-life 65 days

Type of Decay Negative Beta

Molecular Wt. 95 Melting Pt. 1852C Boiling Pt. 3578C

Density 6.49 gm/cc

Structural Formula

$_{40}Zr^{95}$

Specific Power 111 watts/gm

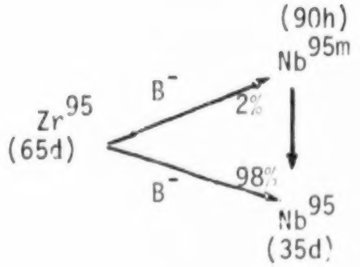
Specific Activity 2.12×10^4 curies/gm

Solubility

Cold Water Insoluble Hot Water Insoluble

Others: Soluble in HF and aqua regia, slightly soluble in acid

Decay Chain



Radiation Energy Level & Intensities

Beta: 0.99 Mev (2%)
0.396 Mev (55%)
0.360 Mev (43%)

Gamma: 0.724 Mev (49%)
0.756 Mev (49%)

Shipping Regulations Classified as a transport group III radionuclide by the Department of Transportation

Comments

References: (1) 776
(2) 2150
(3)

HAZARDOUS WASTES PROPERTIES
WORKSHEET

Name Niobium-95

Half-life 35 days

Type of Decay Negative Beta

Molecular Wt. 95

Density 8.57 gm/cc

Structural Formula

$_{41}Nb^{95}$

Melting Pt. 2468C

Boiling Pt. 4927C

Specific Power 190 watts/gm

Specific Activity 3.93×10^4 curies/gm

Solubility

Cold Water Insoluble

Hot Water Insoluble

Others: Soluble in fused alkali; insoluble in HCl, HNO_3 and aqua regia

Decay Chain

$$\underset{(35d)}{Nb^{95}} \xrightarrow{B^-} \underset{(stable)}{Mo^{95}}$$

Radiation Energy Level & Intensities

Beta: 0.160 Mev (99%)
0.924 Mev (1%)
Gamma: 0.765 Mev (100%)

Shipping Regulations Classified as a transport group IV radionuclide by the Department of Transportation

Comments

References: (1) 776
(2) 2150
(3)

TABLE 1

ANNUAL PRODUCTION OF ZIRCONIUM-95 FROM THE CIVILIAN NUCLEAR POWER PROGRAM 0705

Light-Water Reactor Fuels

Annual Production	Calendar Year 1970	1980	1985	1990	2000	2020
grams/year	$.0128 \times 10^4$	7.31×10^4	13.2×10^4	14.9×10^4	11.8×10^4	39.7×10^4
curies/year	$.272 \times 10^8$	15.5×10^8	27.9×10^8	31.6×10^8	25.0×10^8	73.6×10^8
watts/year	$.142 \times 10^6$	8.11×10^6	14.6×10^6	16.5×10^6	13.1×10^6	38.5×10^6

Fast-Breeder Reactor Fuels

Annual Production	Calendar Year 1970	1980	1985	1990	2000	2020
grams/year			3.54×10^4	21.3×10^4	91.1×10^4	274×10^4
curies/year			7.50×10^8	45.2×10^8	193×10^8	580×10^8
watts/year			3.93×10^6	23.7×10^6	101×10^6	304×10^6

TABLE 2

ANNUAL PRODUCTION OF NIOBIUM-95 FROM THE CIVILIAN NUCLEAR POWER PROGRAM[0705]

Light-Water Reactor Fuels

Annual Production	Calendar Year 1970	1980	1985	1990	2000	2020
grams/year	$.012 \times 10^4$	6.54×10^4	11.8×10^4	13.3×10^4	10.6×10^4	31.1×10^4
curies/year	$.45 \times 10^8$	25.7×10^8	46.3×10^8	52.4×10^8	41.5×10^8	122×10^8
watts/year	$.22 \times 10^6$	12.3×10^6	22.2×10^6	25.1×10^6	19.9×10^6	58.6×10^6

Fast-Breeder Reactor Fuels

Annual Production	Calendar Year 1970	1980	1985	1990	2000	2020
grams/year			2.42×10^4	14.6×10^4	62.2×10^4	187×10^4
curies/year			9.50×10^8	57.2×10^8	244×10^8	734×10^8
watts/year			4.56×10^6	27.5×10^6	118×10^6	353×10^6

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TABLE 3

ACTIVITY OF ZIRCONIUM-95 PRODUCTS IN SPENT REACTOR WASTES 0705

Light-Water Reactor Fuels
(Fuel Exposed to 33 MWD/Tonne* at 30 MW/Tonne)

Fission Products		After 1 year			After 10 years	
	Grams/Tonne	Watts/Tonne	Curies/Tonne	Grams/Tonne	Watts/Tonne	Curies/Tonne
Zr^{95}	1.3	146	28,000	0	0	0
Other Fission Products	35,099	9,854	2,194,000	35,100	1030	317,000

Fast-Breeder Reactor Fuels
(Fuel Exposed to 33 MWD/Tonne at 58 MW/Tonne)

Fission Products		After 1 year			After 10 years	
	Grams/Tonne	Watts/Tonne	Curies/Tonne	Grams/Tonne	Watts/Tonne	Curies/Tonne
Zr^{95}	630	310	59,000	0	0	0
Other Fission Products	34,897	13,490	3,371,000	34,900	776	281,000

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*Tonne is a metric ton of reactor fuel

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TABLE 4

ACTIVITY OF NIOBIUM-95 PRODUCTS IN SPENT REACTOR WASTES 0705

Light-Water Reactor Fuels
(Fuel Exposed to 33 MWD/Tonne* at 30 MW/Tonne)

Fission Products	After 1 year Grams/Tonne			After 10 years Grams/Tonne		
	Grams/Tonne	Watts/Tonne	Curies/Tonne	Grams/Tonne	Watts/Tonne	Curies/Tonne
Nb^{95}	2	285	59,000	0	0	0
Other Fission Products	35,098	9,715	2,163,000	35,100	1030	317,000

Fast-Breeder Reactor Fuels
(Fuel Exposed to 33 MWD/Tonne at 58 MW/Tonne)

Fission Products	Grams/Tonne	After 1 year Watts/Tonne	Curies/Tonne	Grams/Tonne	After 10 years Watts/Tonne	Curies/Tonne
Nb^{95}	3	600	125,000	0	0	0
Other Fission Products	34,897	13,200	3,305,000	34,900	776	281,000

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*Tonne is a metric ton of reactor fuel

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TABLE 5

RADIATION PROTECTION STANDARDS FOR INDIVIDUALS AND POPULATION GROUPS FOR EXTERNAL AND INTERNAL EXPOSURE [2149]

Type of Exposure	Dose to Individuals at Points of Maximum Probable Exposure (rem per year)	Average Dose to a Suitable Population Sample (rem per year)
Whole body, gonads, or bone marrow	0.5	0.17
Thyroid or bone	1.5	0.5
Bone (alternate standards)	Body burden at 0.003 micrograms of radium 226 or its biological equivalent	Body burden of 0.001 micrograms of radium 226 or its biological equivalent

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Table 6

ZIRCONIUM-95 AND NIOBIUM-95 ENVIRONMENTAL RELEASE RATES[2149]

Isotope	Exposure Group	Form	Concentration in Air microcuries/milliliter	Concentration in Water microcuries/milliliter
Zirconium-95	Individual	Soluble	4×10^{-9}	6×10^{-5}
Zirconium-95	Individual	Insoluble	1×10^{-9}	6×10^{-5}
Zirconium-95	Population	Soluble	1.3×10^{-9}	2×10^{-5}
Zirconium-95	Population	Insoluble	$.33\times10^{-9}$	2×10^{-5}
Niobium-95	Individual	Soluble	2×10^{-8}	1×10^{-4}
Niobium-95	Individual	Insoluble	3×10^{-9}	1×10^{-4}
Niobium-95	Population	Soluble	$.67\times10^{-8}$	$.33\times10^{-4}$
Niobium-95	Population	Insoluble	1×10^{-9}	$.33\times10^{-4}$

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